

# Naval Research Laboratory

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## Nanoscience and Nanotechnology

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May 5, 1992

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13. ABSTRACT (Maximum 200 words)  This document reviews the research area of nanoscience/nanotechnology, both within and outside of NRL. Rapid developments in frontiers related to miniaturization have taken place in the last several years, in microelectronics and microelectronic devices, optical materials, biotechnology, structural materials, tunneling tip microscopy (and the field of proximal probes), and microelectromechanical systems (MEMS). Important developments are expected for electronics and computers, sensors, materials, biological behavior, and a number of devices. An overview of these areas is preliminary to examining priorities for investment in this field. This document is an attempt to provide an overview of these diverse efforts, particularly where the Naval Research Laboratory has significant interests.				
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The scope of a brief review of the entire area of nano-science and technology is broader still. Nevertheless, it is anticipated that some coverage of the general subject along with a more thorough but brief exposition of the work at NRL will be of use to those pursuing related research at the Laboratory.

A number of researchers provided contributions to this document. They are recognized in Appendix I along with a mention of their particular area of expertise. Their patience in discussing the ideas contained herein, along with further suggestions which have been made, is truly appreciated.

A tabulation of facilities associated with the nanoscience and nanotechnology effort at NRL is given in Appendix II.

# Preface

This document was prepared as an introductory phase of strategic discussions at the Naval Research Laboratory. It serves to outline a number of activities within and outside of NRL in the field of nanostructures. It is recognized that this field is gaining interest rapidly, and some coordination (or at least communication) among the various elements pursuing this fascinating field at NRL is highly desirable and synergistic.

Rapid developments in frontiers related to miniaturization have taken place in the last several years. Microelectronics is pressing for smaller devices. Optical materials and devices are now made with nanometer-sized components of matter. Biotechnology is utilizing self-assembly for the growth of nanometer patterns. Particulates are prepared for stronger and more versatile mechanical materials. The recent discovery of tunneling tip microscopy (and the field of proximal probes) is adding a powerful fabrication and characterization tool to many of the frontiers involved with nanometer dimensions. Further, the fabrication of mechanical systems involving motors, gears, valves, actuators, etc. is advancing to micron dimensions. Many of the techniques utilized for fabrication and characterization among these diverse frontiers utilize common facilities and/or procedures. This document is an attempt to provide an overview of these diverse efforts, particularly where the Naval Research Laboratory has significant interests.

Any discussion of a topic as broad and encompassing as nanoscience/nanotechnology must necessarily be cursory in many respects. The definition of the subject is somewhat ambiguous - does one include all structures less than one micron in dimensions? To do this would include the entire world of chemistry. Generally speaking, nanostructures are considered to be well-defined structures consisting of many atoms or molecules having dimensions from 1 to 100 nm. This excludes substances such as amorphous organic polymers which involve long molecular chains having these dimensions. However, crystallized and ordered polymeric materials may well be considered to be part of the nanoscience/nanotechnology field.

A linear extrapolation of microelectronics clearly deals with structures which are sub-micron in dimensions. Indeed, 0.25 micron technology is in the near future with this industry. Thus discussion of such devices in microelectronics will be minimized in this document. The frontier involving scientific developments extends to smaller dimensions in this area. However, in the case of micromachines, dimensions are reaching microns in size, and this represents the frontier (discussed in this document) for this particular field. The assumption for this document is that those aspects representing frontier developments in making, measuring, and utilizing smaller bits of matter (larger than a molecule) are to be included for overview.

A special issue of the IEEE<sup>1</sup> covers a number of the frontier aspects of nanoelectronics. The editor, in his introduction to this issue, wrote: "Despite my invitation to do so, no one undertook the tough task of writing an overall review of the subject; however two of the papers provide good reviews of the work at well known laboratories;..." Clearly the entire subject of nanoelectronics is a vast subject in itself.

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<sup>1</sup> Proceedings of the IEEE, 79, (8), August (1991).

# NANOSCIENCE AND NANOTECHNOLOGY

## I. INTRODUCTION

New phenomena and device behavior associated with materials having nanometer dimensions have been pursued through several relatively independent communities over the past decade or so. The communities which have been most concerned about the consequences of materials having sub-micron dimensions include the microelectronics community, the materials community concerned with the strength of structural materials, and the community interested in fabricating and measuring the properties of thin films (magnetic and electromagnetic properties). More recently, the bioscience/biotechnology community has recognized the importance of self-assembly in fabricating structures derived from molecular forces. A dramatic breakthrough in the ability to characterize materials at an atomic level as well as to fabricate materials having nanometer dimensions was introduced with the advent of the Scanning Tunneling Microscope (STM). Tunneling tip technology is having a profound impact on the more conventional communities associated with nanometer dimensions. It is beginning to be difficult to determine which communities exist, as the tunneling tip has introduced such a large and growing following which is having a major impact on the more traditional communities. This technique appears to hold promise of fabricating and characterizing nanoelectronic structures and devices, of measuring nanodimensional properties of magnetism and superconductors, of characterizing molecules and/or associations of molecules on a surface, of characterizing the nanodimensional properties of metals and alloys, and of even revealing fundamental information associated with the science of friction and wear. There is likely to be a substantial impact beyond those areas just mentioned. The time is ripe to assess our current programs and note the impact of this infant field, with an eye to enhancing the future programs in light of new discoveries. The future will be unpredictable, however it seems clear that the areas of opportunity are changing and should be assessed.

The enthusiasm with which nanoscience/technology has been received lately is illustrated by a quote which could be labelled as "imaginative" or "visionary" depending on what future developments actually bring:

"There's no doubt in my mind that nanotechnology and nanoscience will be to the 21st century what genetic engineering has been to the last two decades of this century and probably more. We're going to see nanoscale motors, wheels, gears, computers, you name it. Specially designed nanovehicles will chug through our arteries scouring plaque. Nanosensors and nanodrug-release devices will anchor themselves to vital organs to control and heal them. A computer in the brain. Why not? And all that is only on the human level. In industry, nanotechnology will give us self-replicating machines and parts and faster, cheaper, more complex computing power."<sup>1</sup>:

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Manuscript approved May 1, 1992.

<sup>1</sup>C. Joslin, Trends, Forecasts, and Analyses, Inside R&D, 20, No. 35, pg. 2 (1991) (Technical Insights, Inc., Englewood, NJ).



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A moderating view is appropriate when it is recognized that it may be decades or longer before some of the ideas in this quote have any hope of reaching fruition.

A number of recent reviews and general interest articles on the general subject of miniaturization as a frontier have appeared. The importance of examining this area of research has been recognized in a recent Congressionally-sponsored study<sup>2</sup>. A Physics Today article<sup>3</sup> gives a concise overview of many of the phenomena and challenges of this field. A recent review article<sup>4</sup> gives a general overview of some elements of nanotechnology. A committee of the National Materials Advisory Board has recently published a review<sup>5</sup> of the properties of sub-crystalline materials, with an emphasis on the mechanical properties of these materials. Proceedings of conferences related to electronic properties of nanometer-sized structures have appeared<sup>6,7,8</sup>. Books are appearing which review the subject, particularly the area of

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<sup>2</sup> Miniaturization Technologies, Office of Technology Assessment, Congress of the United States, November 1991.

<sup>3</sup> H. I. Smith and H. G. Craighead, Nanofabrication, Phys. Today, pp 24-30, February (1990).

<sup>4</sup> A. Franks, J. Phys. E: Sci. Instrum. 20, 1441-1451(1987). Nanotechnology.

<sup>5</sup> Research Opportunities for Materials with Ultrafine Microstructures, National Materials Advisory Board, NMAB-454, National Academy Press, Washington, D.C., 1989.

<sup>6</sup> M. A. Reed and W. P. Kirk, Nanostructure Physics and Fabrication, Proceedings of the International Symposium, College Station, Texas, March 13-15, 1989, Academic Press, N.Y., (1989). BOOK - NRL Library QC 176.8 .E4 N32 (1989).

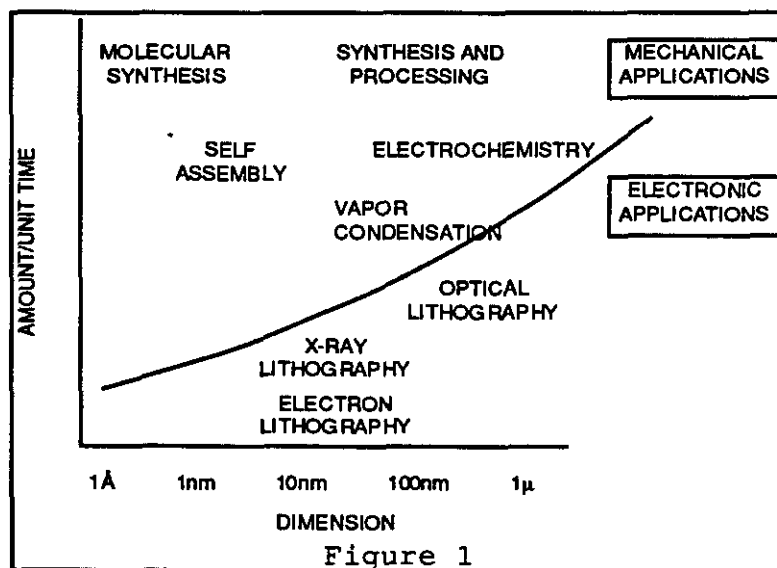
<sup>7</sup> H. G. Craighead and J. M. Gibson, Nanostructures and Microstructure Correlation with Physical Properties of Semiconductors, SPIE - International Society for Optical Engineering, Bellingham, Wash., V. 1284 (1990); Conference 20-21 Mar. 1990, San Diego, CA. NRL Library QC 610.9 .N34 1990.

<sup>8</sup> D.J. Whitehouse and K. Kuwata-Editors, Nanotechnology, Proceedings of the Joint Forum/ERATO Symposium held at Warwick University, 23-24 August 1990. Adam Hilger, N.Y. ISBN 0-7503-0132-5.

## I. INTRODUCTION

physical phenomena associated with mesoscale structures<sup>9,10,11</sup>. The explosively expanding field of proximal probes is the subject of symposia at a number of international meetings<sup>12</sup>. Atomic and molecular manipulation for the fabrication of nanostructures is the subject of a recent Science issue<sup>13</sup>.

Broad sweeping generalizations may be made as illustrated in Figure 1, which indicates estimates for the rate of preparation for a variety of microscopic/nanoscale materials. In general, the smaller the dimension of the particle fabricated, the slower the process. Certainly this is true for lithographic techniques.



<sup>9</sup> F. Capasso, Physics of Quantum Electron Devices, Springer-Verlag, NY, (1989). ISBN 3-540-51128-8; NRL Library QC 688.P48 (1989).

<sup>10</sup> B. L. Atshuler, P. A. Lee, and R. A. Webb, Mesoscopic Phenomena in Solids, North-Holland (Elsevier Science Publishers B.V.) The Netherlands, ISBN: 0 444 88454 8 (1991).

<sup>11</sup> M. Reed, Nanostructured Systems (v.35 of Semiconductors and Semimetals), Academic Press, NY, ISBN: 0-12-752135-6(v.35), (1992).

<sup>12</sup> e.g., the Fifth International Conference on Scanning Tunneling Microscopy/Spectroscopy and the First International Conference on Nanometer Scale Science and Technology, American Vacuum Society, Baltimore, MD, 23-27 July (1990).

<sup>13</sup> Science, 254, 1300-1341 (1991).

## **II. MATERIALS AND FABRICATION**

In any program investigating the behavior of new devices, the beginning of innovation is frequently based on new materials and new techniques for fabricating these materials in specific forms. This is particularly true with the subject of nanoscience/nanotechnology, as the major challenge is simply to obtain the material and/or device on which to pursue experiments. The fabrication of nanostructures which are well characterized constitutes a critically important aspect of the entire subject. Such endeavors are frequently not appreciated in proportion to their importance.

### **A. SEMICONDUCTOR MATERIALS** (Codes 4600, 6800)

Any discussion of semiconductor materials in this document is overtaken by the wealth of literature on the subject. Suffice it to say that the flexibility of semiconductors for engineering the properties needed for electronic circuits appears to exceed almost any other materials considered for this purpose. With the huge industrial network involved with advancing the state of the art for semiconductors, it is clear that NRL programs must reflect specific aspects of semiconductor behavior not generally pursued by industrial organizations in their quest for production items.

Characteristics of semiconductor materials prepared for electronic applications include:

- Low surface dislocation density
- Lattice parameters matching those of epitaxial layers
- Well characterized and controlled defects
- Ability to produce large diameter wafers in volume
- Well controlled surface topographies
- Low cost

The demands placed on semiconductor materials by the nanodimensional world are extreme due to the uniformity of materials and interfaces required. Major materials fabrication problems are encountered due to the migration of atoms just one or two layers from "perfection." As the world of smaller dimensions proceeds on the linearly-extrapolated world of microelectronics, the demand on materials increases dramatically.

The fabrication and utilization of artificially-structured semiconducting materials has become a major objective. About one-quarter of the entire semiconductor physics community is now engaged in studying aspects of layered semiconductor structures. The flexibility obtained by "band gap engineering" with these layered structures along with the increased mobility of carriers in the alternating layers provides considerable enhancement for device performance.

## II. MATERIALS AND FABRICATION

Advances required for monolithic circuits<sup>14</sup>:

Process science (dimensional control and yield)

Device physics (addressing low power dissipation, low noise, and minimized parasitics)

Circuit architectures and function (massively interconnected device functions)

### B. FILM GROWTH (Codes 6345, 6800)

#### 1. EPITAXIAL GROWTH (Code 6800)

Epitaxial film growth techniques such as Molecular Beam Epitaxy (MBE) and Chemical Vapor Deposition (CVD) ushered in the era of reduced dimensionality physics<sup>6</sup>. Monolayers and heterojunction interfaces involving only a few interatomic layers can be grown with good control and reproducibility. A large variety of transport and optical properties can be designed through modification of sample dimensions, lattice matching, and strained layer combinations<sup>15</sup>. The term "bandgap engineering" has resulted from this endeavor.

The techniques of MBE are well developed, and in more recent years emphasis has been in gaining a deeper understanding of the atomistic processes which lead to desired material properties such as atomic smoothness between layers. A number of instrumental techniques are utilized for such investigations. Techniques used to examine the growth of successive layers include Reflection High-Energy-Electron-Diffraction, (RHEED) and photoluminescence (PL).

Associated with the growth of layers for heterojunction material are the difficulties of atomically smooth layers. The kinetic behavior of gases and adsorbed species on the surface as a function of the many parameters associated with the process represents a complex array of variations to be explored in the quest of optimizing the material obtained. A variety of surface-specific diagnostic techniques are employed for this purpose.

### NRL

NRL has a number of activities involving epitaxial growth with MBE (see, for example, Appendix II). Major questions being pursued at NRL include the basic mechanism by which epitaxial layers are initiated, the roughness of the layers, transport of atoms within the layers, and the conditions necessary to grow optimum material.

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<sup>14</sup> Future Prospects for Electronics in Nanometer Structures, G. M. Borsuk, Naval Research Reviews, No. 2, pp 2-10 (1987).

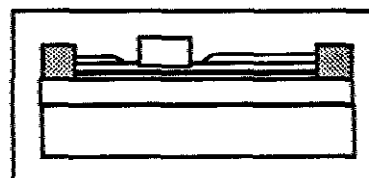
<sup>15</sup> F. Capasso, Physics of Quantum Electron Devices, Springer-Verlag, NY, (1989).

## II. MATERIALS AND FABRICATION

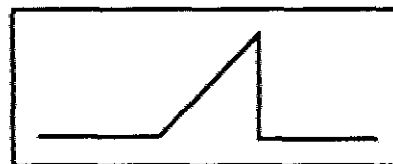
The growth of epitaxial layers of dissimilar materials represents a difficulty if the lattice matching parameters are not exactly coincident (which is almost always the case). Larger crystal sizes introduce greater strain and a greater probability of introducing dislocations and imperfections. One idea which could be utilized in selected circumstances is to grow epitaxial layers on patterned surfaces. If such growth were to take place on 10-100 micron "mesas," the strain introduced over the distance of a mesa would be substantially less. For light-emitting diodes, for example, this idea could be quite useful.

GaAs grown at low temperatures (e.g., 400° C) has interesting properties such as high resistivity. Such material may be used for buffer layers in transistors to cut down leakage currents.

Heterojunction materials are also being applied to microwave and millimeter wave transistors. For low noise applications the High Electron Mobility Transistor (HEMT) (or MODFET) configuration is especially attractive. Devices employing InP (rather than the more conventional GaAs) substrates have been shown by General Electric, Hughes and others to exhibit very low noise at millimeter wavelengths but have severe power limitations. NRL is developing techniques to overcome these limitations. In general InP-based devices are expected to considerably outperform (higher gain, lower noise) GaAs-based devices at millimeter wave frequencies with comparable output power.



By grading the aluminum in GaAs/AlGaAs layers it is possible to get a rectifying barrier similar to a Schottky barrier. Since the Schottky barrier, a simple junction between a metal and a semiconductor, has frequency and power limitations, such an engineered rectifying junction utilizing graded semiconductor interfaces might offer significant advantages. Analysis and experiments are underway at NRL to verify this hypothesis.



Silicon is the most widely used semiconductor in military electronic integrated circuits today, and will continue to be into the future. Because of the relative ease of processing, device designers prefer to work with silicon unless the function they wish to achieve can only be realized in another material. While military silicon devices benefit from the multi-billion dollar investment in the commercial silicon IC industry, current civilian research is focussed towards the development of high density integrated circuits at low cost. But recent advances in nonequilibrium growth techniques, such as molecular beam epitaxy (MBE), and the fabrication of Si/Ge heterostructures offer the exciting possibility of extending silicon-based devices into the high frequency, optical, and nanometer realm. The report from IBM of a Si/Ge heterojunction bipolar transistor showing unity gain-bandwidth product of 75 Ghz at room temperature and of 94 Ghz at 77 K and the announcement from Bell Labs of a Si/Ge HEMT structure with electron mobilities greater than 120,000 cm<sup>2</sup>/Vs at 4 K have

## II. MATERIALS AND FABRICATION

thrust Si-based devices into a regime previously occupied by GaAs-and InP-based devices. The report from JPL of a Heterojunction Internal Photoemission (HIP) device based on the lower bandgap of SiGe alloys and the band offset when a Si/Si<sub>1-x</sub>Ge<sub>x</sub> heterostructure is formed, which has absorption from 2-12  $\mu\text{m}$  with a quantum efficiency of 5% (at 2 $\mu$ ) - 0.2% (at 12 $\mu$ ), respectively, has put Si-based devices into a militarily important infrared realm. Finally there is the frontier area of low dimensional structures (quantum wells, superlattices, quantum wires, and quantum dots) composed of Si/Ge, whose electrical/optical properties might lead to an efficient Si-based laser. But all of these structures are based upon the defect free growth of doped layers of Si<sub>1-x</sub>Ge<sub>x</sub>, for values of x from 0 to 1, on Si, for which there is a lattice mismatch of as large as 4.17%. At the present time there are active research programs in controlled doping (n and p type) during MBE growth, growth of strained-layer superlattices of Si/Si<sub>1-x</sub>Ge<sub>x</sub>, and the segregation of Ge during Si<sub>1-x</sub>Ge<sub>x</sub> growth. The quantum structures are based on the positional control of Ge and the electrical dopants in Si at the atomic level. Devices are being fabricated at NRL which will examine the quantum transport behavior using SiGe materials. This will provide additional information about the band structure of the materials in these devices. This introduces many research issues not being addressed at this time. NRL is the only DOD laboratory investigating the MBE growth of Si<sub>1-x</sub>Ge<sub>x</sub>.

There appears to be a growing recognition at NRL of the importance of carefully characterized materials as a basis for the numerous subsequent activities associated with film growth, in particular. The complexities of how heterojunction materials grow and are characterized requires advanced instrumentation and techniques which are major undertakings. NRL may in fact establish a niche for itself if it can grow truly smooth surfaces. Some characterization techniques such as photoluminescence suggests that NRL has grown the best GaAs/AlGaAs in the world<sup>16</sup>. Increased emphasis and care seems appropriate in this area of research at NRL.

Growth of Ga<sub>0.6</sub>In<sub>0.4</sub>Sb/InAs superlattice material in the Epi-Center represents a current NRL effort to make narrow band gap materials through sophisticated band gap engineering. By making the layers some 25Å apart, the correct energy gap configuration is calculated to give important materials for narrow band gap applications in IR detectors. Good material growth and characterization appear to be important problems to be overcome to make this effort successful.

One of the efforts utilizing the Epi-Center is the fabrication and characterization of an AlSb/InAs/AlSb heterostructure in which the InAs is some 150Å in dimensions. The carrier mobility for the InAs layer in this material has been observed to be 250,000 cm<sup>2</sup>/volt-sec at cryogenic temperatures and 20,000 cm<sup>2</sup>/volt-sec at room T. This behavior suggests interesting high frequency applications if such materials can be fabricated into appropriate devices.

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<sup>16</sup> D. Gammon, B. V. Shanabrook, and D. S. Katzer, Phys. Rev. Lett. **67**, 1547 (1991).

## II. MATERIALS AND FABRICATION

### 2. ELECTRON BEAM DEPOSITION (Code 6340)

By focussing an electron beam onto a metallic surface, sputtering and/or evaporation takes place, depositing a film of the metal on an adjacent surface. This method is used to produce atomically thin films of magnetic materials.

### 3. PULSED LASER DEPOSITION (PLD) (Code 4670)

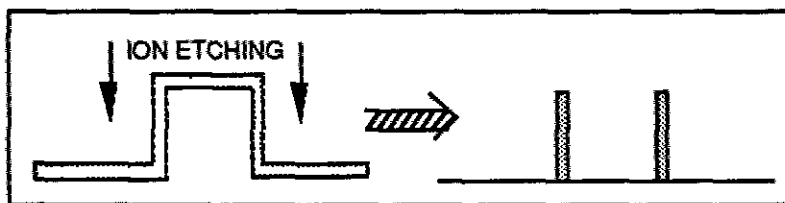
The technique of pulsed laser deposition (or laser ablation) produces high quality films. This is particularly useful for the production of high temperature superconductor materials and films deposited by PLD have been patterned for microwaver delay lines and other device applications. High quality films of ferroelectrics (useful for optoelectronic applications and non-volatile memory) and ferrites (microwave applications) have been deposited. These are patterned by modifications of conventional processing techniques and should be applicable to a variety of devices based on nanotechnology.

### 4. CHEMICAL VAPOR DEPOSITION (CVD) (Codes 6100, 6800)

The CVD technique represents a successful approach to depositing metallic and/or semiconducting films on a surface. The technique is finding wide-spread acceptance in industry.

#### NRL:

NRL is pursuing innovative opportunities with CVD in novel situations. For example, by decomposing metallic precursors under threshold conditions at very low pressures, it is found that highly pure 50 nm layers of platinum can be plated on silicon patterns<sup>17</sup>. By



subsequent ion-assisted etching of these layers using vertically oriented ion beams, 50 nm walls remain. The dimensions have been recently reduced to 35 nm, and further reductions in dimensions appear possible. The vertical components of the original pattern become high resolution patterns for applications such as field emitter arrays, etch masks, X-ray masks, quantum wires, and diffraction gratings. This study is part of the Nanoelectronics ARI at NRL.

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<sup>17</sup> D. S. Y. Hsu, 50 nm linewidth platinum sidewall lithography by effusive-source metal precursor chemical deposition and ion-assisted etching, Appl. Phys. Lett. 59, 2192-2194 (1991).

## II. MATERIALS AND FABRICATION

### C. METALS, ALLOYS AND CERAMICS (Code 6300)

Metals, alloys, and ceramics have been made for decades for mechanical applications in which increased strength has been the goal. These techniques have been described by Ayers<sup>18</sup> in a recent review of the subject. His categorization is as follows:

<u>METHOD</u>	<u>TYPICAL SIZES</u>	<u>COMMENTS</u>
Melt fragmentation		
Gas atomization	~ 10 $\mu$	
Liquid atomization	~ 10 $\mu$	Non-spherical particles
Centrifugal processes	1 - 50 $\mu$	
Emulsification	> 1 $\mu$	
EHD atomization	> 500 nm	
Electrical Discharge	> 2.5 nm	Most particles of micron size
Fragmentation of solids	10 $\mu$ (or less)	
Transformation of solids	> 500 nm	
Precipitation from condensed phases		
Precipitation from liquids	~ 1 $\mu$	
Precipitation from solids		Difficulties in separating powder from solid
Condensation from vapors		
Physical vapor condensation	10 - 1000 nm	
Chemical vapor condensation	> 100 nm	

The tabulation of techniques is convenient as an indicator of the variety of approaches which can be utilized in fabricating nanometer-sized particles. NRL programs include a majority of the methods mentioned above.

### D. LITHOGRAPHY

Electronic chips are currently mass produced by using optical lithographic techniques. These techniques allow the production of many circuits in parallel, but the resolution is limited by the diffraction limit of light. There are several promising higher-resolution lithographic technologies under development, for the fabrication of nanostructures, including focussed ion beams, scanning X-Rays, and scanning tunneling lithography<sup>19</sup>. Electron beam lithography is the most frequently utilized for fabricating single structures, but has the drawback that each device or structure

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<sup>18</sup> J. D. Ayers, Fine Particles, Elliott Symposium Proceedings, pg. 273 (1990).

<sup>19</sup> D. R. Allee, A. N. Broers, and R. F. W. Pease, Limits of Nano-Gate Fabrication, Proc. IEEE 79, 1093-1105 (1991).



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must be fabricated serially (i.e., not in parallel). Scanning tunneling microscopy has the potential resolution equal to or greater than that of electron beam lithography, but alignment and registration problems must be resolved. The means by which these techniques could be used for parallel production of devices is not yet clear.

### 1. ELECTRON BEAM LITHOGRAPHY (Code 6090, 6800)

Electron beam lithography is used to produce high quality high resolution images. These images are currently limited to serial production (i.e., one at a time) of each line in the image, hence the process is slow to produce a complex pattern involving millions of gates. It is utilized in manufacturing primarily to produce the masks used in processes which involve parallel production of the multiple features in a digital image.

The limits of fabricating gates has been explored in recent articles<sup>19,20,21</sup>. Stanford has fabricated gate lengths down to 65 nm, and are entering into consortia to fabricate modulation doped field effect transistors (MODFETs) with gate lengths down to 20nm.

Scanning Electron Beam Lithography (SEBL) is the most widely used high resolution lithographic technique for serial production. The resolution of advanced e-beam lithography tools is not simply the spot size of the focused beam. Electron scattering in the resist and from the substrate exposes the resist over a greater area than the beam spot size. Correcting for these effects (where possible) is computationally intensive and time consuming. A particular problem is compensating for overexposure by backscattered electrons during exposure of adjacent parts of the lithographic pattern (proximity effects). The push to smaller dimensions is concentrated on controlling and understanding these phenomena rather than focussing to a smaller spot. Current wisdom suggests that increasing the energy of the electron beam will provide significant advances. This reduces scattering in the resist and creates a more diffuse fog of backscattered electrons from the substrate. However, correction for proximity effects remains a significant problem particularly for mask making. Current state of the art tools employ voltages up to 100 kV and are necessarily complex and expensive, costing over \$2M. An alternate approach pursued by several groups (notably at NRL and Stanford University) is to go to extremely low energies at which scattering effects are eliminated or spatially confined. 18 nm is about the limit possible in an organic resist such as Polymethyl-Methacrylate (PMMA) on a bulk substrate. This limit is due to the range of low energy secondary electrons, backscattering and the finite size of resist polymer molecules and can be achieved if the beam has a spot size much less than 18 nm. Such results are typically achieved in very high voltage (>300 kV) converted STEMs.

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<sup>20</sup> H. Ahmed, Nanostructure Fabrication, Proc. IEEE 79, 1140 (1991).

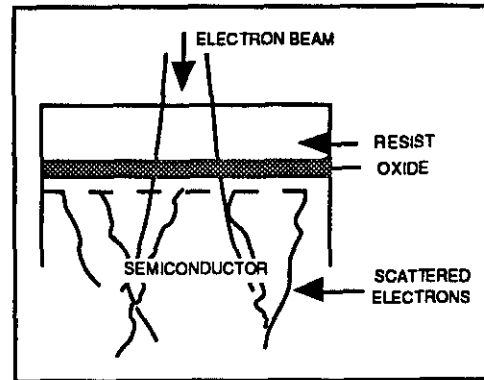
<sup>21</sup> C. R. K. Marrian, E. A. Dobisz, and M. C. Peckerar, Nanostructure Patterning, Proc. IEEE 79, 1149-1158 (1991).

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### NRL:

NRL has some state-of-the-art facilities in electron beam lithography. The JEOL "nanowriter" is capable of focussing an 80Å beam onto a surface. A resolution of some 250Å has been demonstrated with this instrument with the resist PMMA. Using other more technologically useful resists, inferior resolution is obtained. Recent work at NRL suggests that this is related to the problem of backscattered electrons from the substrate exposing the resist away from the area of impact of the primary beam.

An NRL discovery which significantly improves the resolution of a state of the art negative e-beam resist has recently been recognized<sup>22</sup>. This is illustrated in the accompanying figure. A thin dielectric layer between the semiconductor and resist has been found to both reduce minimum feature size and proximity effects. It is believed that charge builds up so the dielectric layer presents a potential barrier preventing low energy backscattered electrons from exposing the resist. This technique has important applications in both direct write and mask making e-beam lithography as it can be used on bulk substrates.



There are some efforts to introduce projection E-beam lithography for electron imaging of an image. This would have the advantage that the pattern could be written in parallel (rather than serial) form. The technique actually focusses the image of an electron beam which has passed through a mask. At present, researchers in this field have not demonstrated much less than 1 micron resolution, indicating some progress, but not sufficient to start a revolutionary movement in that direction.

Another aspect of lithography is that of transferring the pattern created in the resist to the substrate. Techniques such as ion etching or compositional mixing are areas of study at NRL. Emphasis is on the mechanisms of the patterning process, inherent resolution and electronic damage caused by energetic ion etches.

NRL Code 6090 has found that some electroless deposition processes in solution, used for the formation of thin metal films on surfaces, were sensitive to light exposure. This provides a useful procedure for fabricating high-resolution patterns of metal on silicon or other semiconducting material. A variety of metals and sensitive molecular structures have been utilized for this surface-sensitized patterning. This process has reached the stage of demonstrating 0.3  $\mu$  resolution, and is the subject of a Cooperative R&D Agreement with industrial firms. Beyond this

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<sup>22</sup> E.A. Dobisz and C.R.K. Marrian, to be published, J. Vac. Sci. Technol. B 9 Nov/Dec 1991; also, K.W. Rhee, A.C. Ting, L.M. Shirey, K.W. Foster, J.M. Andrews, and M.C. Peckerar, *ibid*).

## **II. MATERIALS AND FABRICATION**

application for semiconductor patterning, the sensitivity of proteins to radiation has been noted, particularly when the protein contains an S-H group. The proteins are released from a chemisorbed surface when irradiated, leaving a surface which does not attract further proteins. The proteins remaining on the surface retain their functional capability. Hence, the possibility exists of fabricating sensors and/or transducers which will convert molecular events to electronic signals for a variety of sensors, including array detectors.

### **2. OPTICAL LITHOGRAPHY**

The common technique for lithographic reproduction of images is that of optical lithography, with wavelengths down to 250 nm have been introduced more recently in order to obtain the higher resolution inherent in the shorter wavelength. The term ("optical lithography") seems to be reserved to techniques utilizing wavelengths longer than 250 nm.

Phase shift lithography is a relatively new idea which offers the promise of better resolution. With phase shift lithographic techniques, "I-Line" techniques have been utilized today to produce MESFETs with 0.22 micron resolution on 3" wafers<sup>23</sup>.

### **3. DEEP UV LITHOGRAPHY**

The terminology of "deep UV lithography" appears to be reserved to lithographic techniques in which the wavelength of the exposing radiation is less than 250 nm. This represents one very important potential direction for nanoelectronic fabrication, and as a minimum represents the near-term direction for industrial production processes.

### **4. X-RAY LITHOGRAPHY**

This form of lithography is gaining a large amount of attention for relatively near-term production of higher-resolution patterns on semiconductors. The minimum resolution for lines from an exposed resist is approximately

$$(\lambda s)^{1/2}$$

where  $\lambda$  is the exposure wavelength and  $s$  is the dimension of the resist. With a resist of 0.1 micron and a wavelength of 10Å, 100Å lines can be expected. This has pointed the direction for some very substantial programs. Typical are the following approximate figures:

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<sup>23</sup> GaAs IC Symposium, Monterey, California, 20-23 October 1991, pg. 281.

## II. MATERIALS AND FABRICATION

DARPA	\$60	M/yr
IBM	\$60	M/yr
Bell Labs	\$10	M/yr
Motorola	\$20	M/yr
Cypress Semi	\$2.5	M/yr

A primary limitation in X-Ray lithography is the lack of a good mask material. Materials such as silicon, silicon carbide, or diamond continue to be explored.

IBM, Fishkill, N.Y. expects to be the first plant to produce products from X-Ray lithographic methods. Their goal is 0.25 micron components utilizing 8Å X-Rays. They are using gold on silicon masks. This is sufficient to make a 256 Mbit DRAM.

### NRL

NRL has had a substantial program in X-Ray lithography for a number of years. Seminal papers and patents were issued more than a decade ago<sup>24,25</sup>. The Memorandum Report contains a number of relevant papers on the subject of X-Ray lithography. The focus of much of this work was on a critical comparison of various sources of X-Rays, the use of point sources of X-Rays from laser-generated plasmas, as well as the limits expected from the use of these techniques.

### 5. TOP SURFACE IMAGING

This term is reserved for lithographic image formation in which the exposing radiation interacts with a thin layer of material at the surface of that which is to be etched or patterned. Exposure by the radiation sensitizes the layer to subsequent processes which serve to differentiate the chemical behavior to the exposed and unexposed regions. The thickness of the resist is not a limiting factor to the resolution achieved. However, subsequent processing methods may well limit the resolution, thus it must be combined with the appropriate processing technique. The lithographic technique mentioned in the subsequent section (in this chapter) on self-assembly is a top surface imaging technique. Other top-surface imaging techniques utilize resists having thicknesses of a micron, resulting in differentiation of the exposed resist through development or further processing.

### 6. RESISTS

The use of resists for the above-mentioned exposure methods is critical. The popular PMMA is a resist having good sensitivity; its characteristics are understood through many years of experimentation and utility. In general, the higher

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<sup>24</sup> R. R. Whitlock, X-Ray Lithography Research: A Collection of NRL Contributions, NRL Memorandum Report 5731, August 24, 1987.

<sup>25</sup> D. J. Nagel and M. C. Peckerar, Pulsed X-Ray Lithography, U. S. Patent No. 4,184,078, Jan. 15, 1980.

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sensitivity a resist, the more granular the image formed. For reference, one photon per  $10^4 \text{ \AA}^2$  in the visible represents approximately 0.5 microjoule of energy per  $\text{cm}^2$ . This is a nominal exposure level for moderately polymerized PMMA. In fact, as a general rule of thumb for most resists, it is desirable to be able to expose about  $10^4 \text{ \AA}^2$  with the incidence of one photon, electron or ion. If a granularity of dimensions smaller than  $100 \text{ \AA}$  is desired, less sensitive resists will be a necessity. Since a nominal molecule dimension covers approximately  $10 \text{ \AA}^2$ , "amplification factors" of 1000 are commonly expected.

### 7. MICROMACHINING

Micromachining has become a field of growing interest during the last several years. Although the field is not, at the present time, producing components which are nanometer in dimension, (5-100 microns is more typical) these efforts represent a frontier for miniaturization processes for the design of mechanical systems. For that reason, some mention of the micromachining state-of-the-art is included in this document.

Micromachining has been stimulated with two notable advances in the '80s:

- 1) In 1983, the development of a sacrificial layer of polysilicon enabled parts which were micromachined to be lifted from the substrate through a hydrazine etch. This allowed researchers to make parts all assembled after etch formation.
- 2) In 1988, the development of the electrostatic motor introduced the source for mechanical motion of gears and rotational motion. The electrostatic motor is possible due to the breakdown behavior of air, which is increasingly more stable to breakdown over distances small relative to the mean free path of gas molecules (the Paschen Curve). The consequence of this is that higher electric fields can be utilized for the armature of micromachines, and the forces associated with these fields become greater than the magnetic dipolar sources typically used for larger electric motors.

A number of imaginative micron-sized mechanical devices have been made in attempts to demonstrate the fabrication capabilities and potential utility of such small mechanical devices. One such example<sup>26</sup> constructs interlocking gears which have axles only 8 microns in dimensions.

Micro-ElectroMechanical Systems (MEMS) represent a relatively new world of machining and miniature systems<sup>27</sup>. Components (gears, motor armatures, membrane

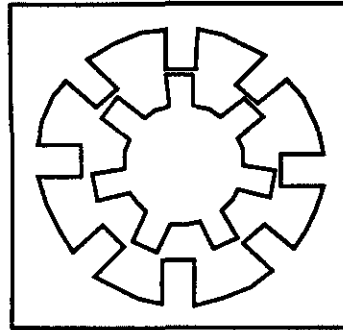
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<sup>26</sup> Dawn of a micromachine age?, Science, 253, 143 (1991). H. Guckel, is the technologist referred to in this clipping.

<sup>27</sup> R. T. Howe, R. S. Muller, K. J. Gabriel, and W. S. N. Trimmer, Silicon micromechanics: sensors and actuators on a chip, IEEE Spectrum, pg. 29-35 (1990).

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pumps, etc.) are typically made with dimensions approaching 3-5 microns in thickness, and 5-100 microns in lateral dimensions. These motors have operated at 15,000 rpm for periods of seven days straight. Forces developed have been about  $10^{-5}$  ntn-m of torque, which is sufficient to overcome the frictional resistance. A process technology called LIGA (Lithografie, Galvanoformung, Abformung) utilizes X-Ray lithography and very thick resists to fabricate silicon components having 80-100 microns thickness.



A recent meeting of the Materials Research Society included mention of a new and novel motor drive for micromachines. A ferroelectric lead zirconate-titanate film on silicon over a diaphragm is used to drive a traveling surface flexure wave which, through friction contact with a micro-gear, drives the gear<sup>28</sup>. This micromotor is reportedly about 1 mm in diameter, and has the advantage of providing significant force as a driver for micro-robots.

Resonant structure motors have been made which oscillate at several hundred kilohertz (there is one which reputedly operates at 1 MHz at Berkeley). With sparsely arranged anchor points connected by springs to the rest of the device, the interdigitated comb capacitors (or Multiple-Interleaved-Plane Actuators, MIPA) are charged to provide the displacement forces. The device rides on a cushion of air. Such devices, at pennies apiece, have shown to be high performance inexpensive accelerometers, and are being introduced into air bag ejection controls for American automobiles.

By making use of the variable etch rate of the various planes of silicon to different processes, precisely defined planes at angles along crystal faces can be machined, providing the means of fabricating groves and cavities in silicon crystals.

One aspect of micromachines which will need examination is the tribological aspects of friction and wear at such small dimensions. It will be difficult if the materials rubbing together are the same material, which is the case in micromachines envisioned today.

Within the concept of micromachines is that of molecular machines. The concept that molecular constructs may be designed to perform specific functions has stimulated considerable speculation and frontier research activity in the biological world. Examples of molecular machines which have evolved from nature include the flagella which propel bacteria. Modification of the DNA of such species already has demonstrated the ability to control the "clock rate" or sense of rotation of these flagella.

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<sup>28</sup> Inside R&D, 20 (51), December 18, 1991. This was accomplished at M.I.T. by A. M. Flynn, A.I. Laboratory.

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### E. PLASMAS AND BEAMS

#### 1. ION BEAMS

##### a. Ion Beam Assisted Deposition (IBAD) (Code 4670)

NRL has made a number of Rugate filters (sinusoidal variation in composition over about 1000Å repetition distances) utilizing this technique. Recently X-Ray mirrors have been fabricated having 25Å layers of SiN (Si/Si<sub>3</sub>N<sub>4</sub>) with 200 pairs of layers of this material. The theoretical reflectivity of this material should be 9%, however due to imperfections and density variations the measured peak reflectivity is currently about 1% (which is still better than the commercial SiN reflectors). Masks for X-ray lithography have also been deposited by IBAD. High current density contacts for GaAs deposited by IBAD are being studied for laser triggered switch applications.

##### b. Ion Beam Etching (Code 4670)

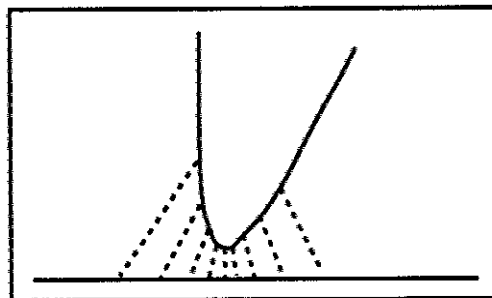
Ion beam etching using ECR is being studied for dry etching of a variety of substrates used in microelectronics.

##### c. Focussed Ion Beam Milling (Code 6345)

A field emission tip which has been wet with liquid gadolinium emits a strong beam of gadolinium ions which can be focussed to spot sizes on the order of 400Å. This device has been set up at NRL, and is capable of milling fairly small patterns on semiconductor substrates. Currently vibrational effects on the order of 1 micron limit the usefulness of the device, but plans are being made to transfer it to a vibration-free mounting in a chamber in the NRL Epi-Center.

### F. FIELD EMISSION TECHNIQUES (Codes 6090, 6100, 6800)

The scanning tunneling microscope (STM) first achieved renown as a tool for imaging the atomic configuration of a surface. It was soon realized that the technology could be used to form a spatially confined low energy electron beam. Such an approach overcomes the problems associated with focussing low energy electrons with conventional electron optical lenses. Low voltage (15-50 V) e-beam lithography in practical resist materials has been demonstrated with STM-type instruments operating in a "field emission" mode by researchers at IBM, NRL and Stanford University. The NRL group report that patterns have been written showing 23 nm



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features in the developed resist<sup>29,30</sup>. Interestingly this is over four times smaller than can be written, on the same substrate in the same resist, with a tightly focused 50 kV e-beam<sup>31</sup>. In this mode, feature size is maintained regardless of pattern geometry indicating an absence of proximity effects. IBM has reported an "STM controlled field emission tip<sup>32</sup>" operating at the low-keV energy range. This system has resolution limits of a scanning electron microscope (SEM). Clearly these results indicate ultra-low voltage lithography can overcome the problems of electron scattering. Furthermore, the resist patterns are sufficiently robust to be transferred into the underlying semiconductor by wet or dry etching showing the technique has technological interest.

The latent image of an e-beam lithographic pattern in an undeveloped polydiacetylene resist (P4BCMU) has been observed with an STM<sup>29</sup>. This was the first high resolution observation of the latent image and demonstrated that the resolution observed in the resist was related to the exposure process rather than the development step, i.e., the latent image was close to the width of the developed resist line. Subsequently researchers at Stanford University have used an AFM to observe the exposure due to backscattered electrons in a latent image in PMMA.

Another intriguing lithographic application of the STM is the selective oxidation of Si and GaAs. Patterns can be written directly onto suitable prepared

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<sup>29</sup> C. R. K. Marrian, E. A. Dobisz, and R. J. Colton, Lithographic studies of an e-beam resist in a vacuum scanning tunneling microscope, *J. Vac. Sci. Technol. A* **8**, 3563-3569 (1990).

<sup>30</sup> C. R. K. Marrian, and R. J. Colton, Low-voltage electron beam lithography with a scanning tunneling microscope, *Appl. Phys. Lett.* **56**, 755-757 (1990).

<sup>31</sup> E.A. Dobisz and C.R.K. Marrian, *Appl. Phys. Lett.* **58** (22), 2526 (1991).

<sup>32</sup> T. H. P. Chang, D. P. Kern, and M. A. McCord, Electron optical performance of a scanning tunneling microscope controlled field emission microlens system, *J. Vac. Sci. Technol.* **V7**, 1855-1861 (1989).



## II. MATERIALS AND FABRICATION

surfaces which are robust enough to withstand dry etching<sup>33,34</sup>. This type of lithography can be performed in air and is an example of chemically modifying materials selectively under the action of the STM tip.

A great virtue of the STM based technique for creating a spatially confined e-beam is its simplicity. Low voltages are employed and the STM design is necessarily compact. In contrast, high voltage electron optic columns for lithography tools are more complex and have greater reliability and maintenance problems associated with their operation at 100 kV or higher.

The STM has also been used to modify surfaces directly. 20 nm features have been created while etching GaAs in solution<sup>35</sup>. The melting of conductive glasses under the action of an STM tip has produced high resolution features<sup>36</sup>. Chemical modification of a Ag<sub>x</sub>Se film has produced 10 nm lines<sup>37</sup>. Field induced diffusion of Cs on GaAs at room temperature has produced areas of high Cs concentration of 1-10 nm size<sup>38</sup>.

Recent chemical vapor decomposition of trimethylaluminum at 10<sup>-4</sup> Torr have

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<sup>33</sup> J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, and J. Bennett, Modification of hydrogen-passivated silicon by a scanning tunneling microscope operating in air, Appl. Phys. Lett. **56**, 2001-2004 (1990).

<sup>34</sup> J. A. Dagata, W. Tseng, J. Bennett, C. J. Evans, J. Schneir, and H. H. Harary, Selective-area epitaxial growth of gallium arsenide on silicon substrates patterned using a scanning tunneling microscope operating in air, Appl. Phys. Lett. **57**, 2437-2439 (1990).

<sup>35</sup> L. A. Nagahara, T. Thundat, and S. M. Lindsay, Nanolithography on semiconductor surfaces under an etching solution, Appl. Phys. Lett. **57**, 270-272 (1990).

<sup>36</sup> U. Staufer, L. Scandella, H. Rudin, H.-J. Guntherodt, and N. Garcia, Tailoring nanostructures with a scanning tunneling microscope, J. Vac. Sci. Technol. B **9**, 1389-1393 (1991).

<sup>37</sup> Y. Utsugi, Nanometer-scale chemical modification using a scanning tunnelling microscope, Nature **347**, 747-749 (1990).

<sup>38</sup> L. J. Whitman, J. A. Stroscio, R. A. Dragoset, and R. J. Celotta, Manipulation of Adsorbed Atoms and Creation of New Structures on Room-Temperature Surfaces with a Scanning Tunneling Microscope, Science **251**, 1206-1210 (1991).

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produced 1 nm structures on graphite<sup>39</sup>. Laser irradiation of the region near the tunneling tip enhances the aluminum deposition<sup>40</sup> (NOTE: this work was supported by NRL).

Perhaps some of the most striking recent experiments have appeared by researchers at IBM, who have successfully trapped a single xenon atom between a surface and a tunneling tip<sup>41</sup> to make a "switch" by alternating the voltage and hence the position of the xenon atom between tip and surface. This single-atom memory is far from a practical device, however it illustrates the potential information density of many orders of magnitude beyond current state-of-the-art commercial digital devices.

One of the more interesting observations made recently by using the Ballistic Electron Emission Microscopy (BEEM) is that electrons from a tunneling tip having energies of only 2-3 volts can modify the lattice structure of materials<sup>42</sup>. The mechanism is not clearly understood, however hypotheses suggest that an ion resulting from a low energy electron beam is not stable in the lattice of neutral atoms. It migrates to a position of new stability in a time short relative to the time required for re-establishment of electrical neutrality. The resultant dislocation is registered as a materials modification.

It is clear today that tunneling techniques represent a powerful tool for exposing surfaces and resists, both alone and in the synergistic way with light, as well as for moving atomic and cluster structures on a surface. The number of potential opportunities for scientific discovery involving phenomena and devices appears to be large.

### G. ELECTROCHEMICAL TECHNIQUES

As electrode dimensions become smaller, they approach the size of tunneling tip probes. There is little distinction between electrochemistry at these dimensions and the usual deposition processes utilizing tunneling tips. Electrochemical aspects at nanometer dimensions are gaining attention as structures built through electrochemical processes approach nanometer dimensions.

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<sup>39</sup> S.-T. Yau, D. Saltz, A. Wriekat, and M. H. Nayfeh, Nanofabrication with a scanning tunneling microscope, J. Appl. Phys. **69**, 2970 (1991).

<sup>40</sup> S.-T. Yau, D. Saltz, and M. H. Nayfeh, Scanning tunneling microscope - laser fabrication of nanostructures, J. Vac. Sci. Technol. B **9**, 1371-1375 (1991).

<sup>41</sup> D. M. Eigle, C. P. Lutz, W. E. Rudge, An Atomic Switch Realized with the Scanning Tunneling Microscope, Nature, **352**, 600-603 (1991).

<sup>42</sup> R. A. Buhrman, School of Applied and Engineering Physics, Cornell University; Private communication.

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### HL SELF ASSEMBLY OF MOLECULAR STRUCTURES (upward engineering) (Code 6090)

The term "self assembly" became popular as a means of achieving nanostructures during the last decade. It involves the natural attraction between atoms and molecules to form small structures. In many respects, the same forces are responsible for condensed phases and crystallization of atomic and molecular substances. However, the process of self-assembly does not in general refer to the great preponderance of condensed phase formation. Rather, it is reserved for the formation of nano- or sub-micron structures which consist of an assemblage of atoms or molecules in rather unique structures. Several atoms or molecules make up such a structure.

There are numerous examples of large biological molecules which bind to one another (antibody - antigen interactions, for example). Medical and/or biological applications of such nanometer structures are not considered to be part of the definition covered here. Some programs in the chemical and biological communities deal with the formation of nanometer-scale geometric structures. Some of these structures are envisioned for use due to unique material properties, and could stimulate the attention of groups interested in materials properties. It is conceivable that ordered nanoelectronic systems of the future could derive from self-assembled arrays. This could be a cost-effective means of creating nanometer structures. The speed and reliability of such systems remain to be demonstrated.

One aspect of self-assembly is pursued with the tunneling tip phenomenon (or small-scale electrochemistry). It has been noted that defects prepared electrochemically move around on a surface. By probing these defects with electrodes they may be made to move, concentrate, or "self-assemble."

The concept of "molecular machining" seems to be gaining some attention. In this concept, the direct interaction of chemical species on a proximal probe with a surface is used to form and break bonds, with the idea of shaping the surface (or molecules) which are interacting. Although this idea is somewhat futuristic in nature, it seems to have generated considerable attention.

The term "Molecular Electronics" was coined when the concept of self-assembly became associated with the very futuristic concept of fabricating logical computing elements. The section on molecular electronics is included here under "fabrication" due to the fact that the majority of efforts related to this today tend to be related to the fabrication aspect of nanoscience. A couple of quotes tell the story:

"In the period 1983 - 1984, some unscientific proposals about self-assembling biological 'computers'; ('biochips') received unfortunate, undeserved and uncritical world-wide media attention; the critical reaction to such exaggerations almost drowned, in the ocean of righteous disbelief, the infant field of [Molecular Electronics - ME] ! A

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very sobering note outlined what technical accomplishments were still needed<sup>43</sup>. Since then, more conservative chemists, physicists, and materials scientists have broadened the definition of ME, relabelled some of their research areas as ME, and thus have given ME its present nascent respectability."<sup>44</sup>

Moore's Law states that the circuit density increases by a factor of four every two years. This has been true since early 1960's.

"By simple extrapolation it will take approximately two decades for electronic switches to be reduced to molecular dimensions. The impact of molecular biology and genetic engineering has thus provided a stimulus to attempt to engineer upwards, starting with the concept that single molecules, each acting as an electronic device in their own right, might be assembled using biotechnology, to form molecular electronic devices (MEDs) or even biochip computers (BCCs)."<sup>4</sup>

"The enzymatic reactions of DNA replication, transcription and translation in biological systems, appear to be nature's closest approach to the elements of computing and dissipate energy amounting to 10-100 kT per primitive step, which compares very favorably with the  $10^{10}$  kT per 'equivalent' programming step in a transistor-based computer; it is the heat dissipation problem which will limit the ultimate micro-miniaturization based on conventional technology (Bennett 1982, Feynman 1985)."

"Self-assembly has come to be regarded as a compelling if not the logical solution to the fundamental problem in molecular electronics of how to fabricate circuitry molecule-by-molecule."<sup>45</sup>

NRL:

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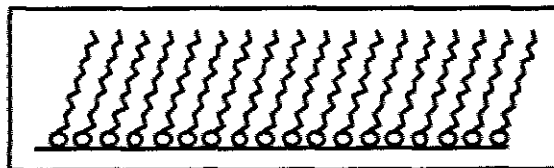
<sup>43</sup> R. C. Haddon, A. C. Lamola, Proc. Natl. Acad. Sci. U.S., **82**, 1874 (1985).

<sup>44</sup> R. M. Metzger, and C. A. Panetta, New J. Chem. **15**, 209-221 (1991).  
The Quest for Unimolecular Devices.

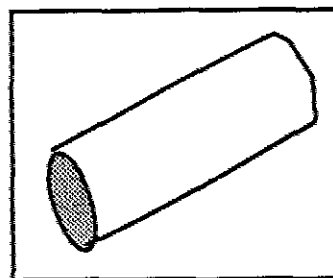
<sup>45</sup> J. S. Lindsey, Self-Assembly in Synthetic Routes to Molecular Devices. Biological Principles and Chemical Perspectives: A Review, New J. Chem. **15**, 153-180 (1991).

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Suitable organic materials, when applied to the surface of a suitable fluid (water being the most common), will spread out to form a monolayer. By collecting this monolayer on a plate, a reasonably well-ordered monolayer of this organic material may be collected. The process may be repeated many times to form many layers, regularly spaced. These films may be characterized by X-ray diffraction as well as with tunneling tip techniques. By utilizing ferroelectric polymers in this process, it is anticipated that the ferroelectric transition temperature may be tuned to be near room temperature. This should give films which are highly sensitive to thermal changes due to absorbed IR radiation, with the goal of fabricating sensitive pyroelectric sensors.



The formation of tubules from the natural attraction of lipid molecules has been pursued for several years at NRL. These tubules have diameters ranging from  $.05 \mu$  to  $3 \mu$ . They form a template for a metal coating process, hence the tubule may be made of organic or metallic materials. The metallic coatings have been found to be somewhat less (factor of 10) conductive than the bulk counterparts. They have been envisioned for a number of potential applications, including inclusion in composites (for strength and dielectric properties), as a microencapsulating medium for controlled release (envisioned in a possible ship hull coating material), and for cold cathodes (the high curvature of the small structure provides high electric fields and efficient electron emission).



An NRL ARI entitled "Molecular Engineering of (Bio)materials and Interfaces" has been initiated on 1 October 1991. Programmatically, this research is in three areas: 1) 2-dimensional molecular engineering, 2) nucleation on patterns, and 3) multilayer structures.

1) 2-Dimensional molecular engineering: This aspect of the ARI is to investigate molecular interactions with photons (UV, X-Ray, etc.), electrons (beams, electron tunneling tips), and atomic force microscopy. Patterns can be introduced with such interactions. What can be done with such interactions, including resolution of such patterns, how can they be characterized, and what does the patterning mean?

2) Nucleation on patterns: Once the patterns are made, what can be placed on the patterns which can be of use for applications such as microlithography? Past successes related to the microlithography program in Code 6090 suggest many opportunities here. It would be useful to know how to tailor the wettability of the surface. Methods involving "top surface imaging" (pioneered by Gary Taylor at Bell Laboratories in the middle 1980's) are advantageous for smooth chip surfaces and higher resolution of the patterns

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produced. The objective here is to work out the chemistry for tools of the future which may be of use in producing nano-patterns.

3) Multilayer structures: The approach envisioned to make multilayer structures involves successive chemisorption on successive surface layers. This approach is favored over other physisorbed methods such as Langmuir-Blodgett films due to the stability of the chemisorbed species. Potential applications anticipated include structures for X-Ray optics, magnetic materials, nonlinear materials, etc.

A further project involves modification of the ideas derived from tunneling tip phenomena. By fabricating a tunneling tip chemically bound to enzyme molecules, it is anticipated that a tool for selectively creating highly localized chemical reactions can be devised as the tip is dragged across a suitably prepared surface. The ability to write patterns in molecular-based substrates is anticipated with such techniques. Potential applications in sensors or lithographic techniques is anticipated once the chemistry associated with the many such variations is better understood.

The possibility of controlling neuron growth in selected patterns is of interest here. Such techniques could be the genesis of building cells which have very selected functions in a living organism (this potential application is some distance in the future). This has shades of the "robot in the bloodstream."

### I. SELF ASSEMBLY OF METALS AND SEMICONDUCTORS (Code 6870)

NIST has formed quantum wires of alkali metals formed as chains on the surface of semiconductors. Through proximal probes, it has been found that the chains are not conducting. The atoms form in the template of the semiconducting substrate with a spacing somewhat greater than in the metal. There appears to be no need of utilizing a terrace for the formation of these alkali metal chains.

Certain semiconducting compositions appear to solidify with self-assembled structures. Materials containing Ga, In, As, and P simultaneously have produced single atomic layers of the elements. InGaAs has produced nodules on the order of 100Å in dimensions.

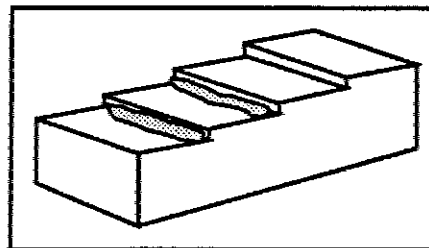
Clusters in inorganic/organic ions in solution can be prepared as chemical compounds. Subsequent decomposition can produce residues containing the semiconductor atoms which were constituents in the ion structures.

### NRL:

Atomic terraces form along faces of crystalline materials which have been fabricated with one face nearly parallel to a major crystalline plane. These atomic steps are favored for additional crystalline growth of either the same material or material which is similar in

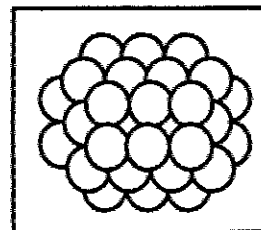
## II. MATERIALS AND FABRICATION

behavior to the base material. The formation of atomic wires along the lines where these atomic steps occur has been demonstrated. NRL research is being pursued in preparing and characterizing such structures. UCSB has a substantial program in this particular line of investigation also.



### I. CLUSTER FORMATION (Codes 6112, 6371)

The formation of clusters involving aggregates of a number of atoms or molecules is the focus of a Core Program in Code 6100. In some sense, the formation of clusters comes in the category of self-assembly, however the simple process of crystallization is not usually associated with the term "self-assembly." The code 6100 group has strong capabilities for making clusters through processes such as laser ablation, and in characterizing them with several different types of mass spectrometry. This technique can be used as a probe to detect unusual species. As an example, the existence of the currently exciting field of fullerenes was initiated by the observation of the surprisingly stable (magic numbers)  $C_{60}^+$  cluster in mass spectrometry. Similar stability has been recently observed with  $Si_{45}^+$ . One aspect of this cluster research at NRL will continue to explore the vastly complex field of permutations giving rise to cluster species. Silicon carbide clusters have been of interest recently due to evidence of the importance of cluster carbide species affecting the performance of silicon devices. It has been hypothesized that tubules of carbon with the basic outer structure of  $C_{60}$  might be obtained through appropriate syntheses. Such structures would have interesting conductive properties, both regular and superconductivity.



The tools associated with cluster formation and measurements could be useful in characterizing properties of interest for both clusters and bulk samples. The chemical reactivity can provide important information about the structural isotopes actually obtained under selected experimental conditions. Certain aspects of passivation can be observed by measuring the chemical activity of silicon clusters or hydrogenated silicon clusters.

More recent aspects of the clusters program are aimed at placing clusters on a surface and characterizing them with some of the new tunneling tools becoming available. Techniques involving cluster scattering behavior from a surface are also of interest.

It would be useful in the future to devise synthetic techniques for producing clusters having a small range of sizes. Cluster synthesis for materials having electronic applications should offer future opportunities. There appears to be a definite opportunity to combine the field of tunneling tips with that of clusters. Bell

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Laboratories have had such programs. The fullerenes offer a vast number of opportunities for studies; selected directions should be pursued here.

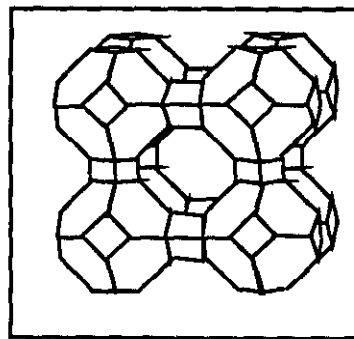
Elsewhere, it has been recently found (by John Weaver at the U. of Minnesota) that a condensed layer of Xe on a silicon surface can reduce the damage done by clusters impinging on a surface, providing superior films and interfaces.

NRL efforts examining the condensed product of argon-sputtered molybdenum have produced surprise structures<sup>46,47</sup>. The basic condensed unit of molybdenum consists of relatively monodisperse 50Å cubes. The surprise which was discovered at NRL is that the basic cubes form larger aggregates involving largely eight and 27 units in the form of larger cubes, built up from the basic aggregates. Future directions for this research include hopes of finding ways to scale up such processes, and the consideration of making ordered arrays for electronic applications. Of course, the mechanism by which these specific cluster formations appear is not understood, and lays the path to interesting scientific questions.

### K. USE OF TEMPLATES (Codes 4680, 6090, 6170, 6321, 6522, 6546)

It seems self explanatory that the introduction of materials into nanometer-sized holes or orifices will produce nanometer-sized inclusions. This method actually has attracted considerable attention in a couple of cases.

The use of zeolites for encapsulating samples is attractive due to the availability of zeolite samples of varied chemical and structural composition. The zeolite structure typically consists of channels having dimensions of from 5-7Å. Some newer synthetic zeolites have channels as large as 25Å. Type L zeolites contain channels which are 1-dimensional in nature (straight). Other types of zeolites contain channels which occupy 2- or 3-dimensions. The dimensionality of intracrystalline diffusion may, thus, be controlled. Zeolites may be filled with metals and/or semiconductors as well as various molecular species, and have been utilized for such behavior in a number of studies.



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<sup>46</sup> A. S. Edelstein, G. M. Chow, E. I. Altman, R. J. Colton, and D. M. Hwang, Self-Arrangement of Molybdenum particles into Cubes, *Science* **251**, 1590 (1991).

<sup>47</sup> R. W. Cahn, Minute Particulars, *Nature* **353**, 208-209 (1991).

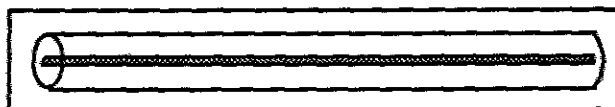


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NRL efforts utilizing the use of zeolites include incorporating them in electrodes, with consequent modification of the chemical reactions associated with the usual electrochemical transformations<sup>48</sup>.

It is also possible to produce 10-100 nm holes in glass by mechanical drawing and subsequent processing. These may be filled using chemical vapor deposition techniques or other procedures to produce quantum wires in a well-characterized environment.

An interesting observation has recently been made at NRL on bismuth which has been drawn into ultra-small capillaries<sup>49,50</sup> (Taylor wires). Through observations which were made using the synchrotron X-ray source at NSLS, Brookhaven, the bismuth which forms in capillaries smaller than (about) 700Å is in a new crystalline form, not previously reported. This new crystalline form may be due to "hoop stress" caused by the expansion of the bismuth upon solidification in the presence of the surrounding glass. Noting that high  $T_c$  superconductivity has been predicted<sup>51</sup> in other materials when formed in filaments of this size, the potential superconducting properties of this new material are being investigated.



A novel technique for producing nanoparticles by making use of self-assembled molecular structures is taking place at NRL. It has been well known that lipids assemble into sub-micron spheres known as vesicles. Likewise, it has been recognized that the stabilization of sub-micron particles in a fluid (a sol) is frequently inhibited by agglomeration of the particles. By preparing the basic particles inside a vesicle (by sonification and subsequent diffusion of the reactants through the vesicle wall, for example) the particles may be prepared with a coating which prevents

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<sup>48</sup> D. R. Rolison, Zeolite-Modified Electrodes and Electrode-Modified Zeolites, Chem. Rev. 90, 867-878 (1990).

<sup>49</sup> E. Pennisi, Synchrotron Beam Sees Record Tiny Crystal, Science News, 140, 164 (1991).

<sup>50</sup> E. F. Skelton, J. D. Ayers, S. B. Qadri, N. I. Moulton, K. P. Cooper, L. W. Finger, H. K. Mao, and Z. Hu, Synchrotron X-ray Diffraction from a Microscopic Single Crystal Under Pressure, Science, 253, 1123-1125 (1991).

<sup>51</sup> Phys. Rev. 39, 4776 (1989).

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agglomeration<sup>52</sup>. Sintering of the resultant material can give fairly pure products with sub-micron particle sizes (40 nanometers has been demonstrated). Many variations are possible and will be examined in this embryonic field. The question of whether metals can be prepared in this manner is currently open to question. Potential applications of materials prepared in this manner include the magnetic recording industry and the preparation of small samples of composites for subsequent testing of the properties.

Other NRL techniques have demonstrated the utility of preparing thin tubules of diamond by a CVD process on metal wires. The NRL tubules prepared in this manner are currently greater than micron dimensions, and the wall sizes have been prepared with 1 micron thickness. This technique is being explored for its limitations at the present time. One potential application which comes to mind is for sleeve bearings on micromachines. The possibility of utilizing such structures for electronic devices or cold cathode emission is being considered.

### L. MECHANICAL AND THERMAL PROCESSING FOR STRUCTURAL MATERIALS (Code 6300)

A major area for the synthesis of nanometer-sized particles of metals and alloys has been that of vapor condensation. Particle sizes of 10-30 nm is common from such processes. The Japanese have done a great deal of work in this area. However little seems to have emerged at the present time in the way of commercially-important products from these techniques. Herbert Gleiter at the U. of Saarland, Germany, has published a number of papers involving synthesis and measurements of the mechanical properties of a number of such materials. "Remarkable" properties are suggested for such properties involving diffusion, elastic moduli, diffraction studies (suggesting a greater degree of disorder than in an amorphous solid), ductility at low temperatures for ceramics, etc.

A traditional approach, used for many years, to obtaining very small particle sizes in metals is that of "dispersion strengthening" by "mechanical alloying." Cold working of, for example, nickel with 1-2% of thorium oxide (thoria) in a ball mill produces very fine nickel grains. Controlled recrystallization results in larger grains with thoria dispersed. This material is important for its higher strength.

Tungsten carbide has been produced for 50 years by introducing 5-20% cobalt in fine carbide particles. The cobalt acts as a "cement." Smaller carbide particle sizes (10 microns; new materials today are emerging with 1 micron particle sizes) has more recently resulted in higher performance materials used in cutting blades industrially. A firm in New Jersey is currently attempting to develop materials using sub-micron carbide particles produced by co-precipitation of the carbide precursor with cobalt.

There is reason to believe that the mechanical properties described above would improve with still smaller particle sizes, however the problem of increased creep with

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<sup>52</sup> H. Liu, G. L. Graff, M. Sarikaya, and I. A. Aksay, Synthesis of Ultrafine, Multicomponent particles using Phospholipid Vesicles, Preprint.

## II. MATERIALS AND FABRICATION

these small particle sizes suggests that there may be somewhat less utility of these materials for high temperature applications.

Other techniques to prepare nanocrystalline metals<sup>53</sup> with grain sizes of 1 to 10 nm include sputtering and rapid solidification methods.

### M. COMPOSITES

Composites consisting of nanometer-sized particles dispersed in a binder are prepared in a great many ways. Metallic and ceramic composites are prepared using techniques such as simple mixing of constituent materials, work hardening of heterogeneous mixtures, and co-precipitation. NRL has many programs associated with these fabrication methods for preparing materials for structural applications.

NRL has also found ways to prepare quantum dots of CuCl and CdS in glass, taking advantage of the exciton absorption in these samples which reveal a narrow resonance in the infrared. The exciton species is present due to confinement effects not evident in the bulk structure of these materials. Fabrication by using a controlled separation of phases through precipitation and annealing of a base glass appears to provide the necessary samples.

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<sup>53</sup> C. Suryanarayana, and F. H. Froes, Nanocrystalline Metals: A Review, Physical Chemistry of Powder Metals Production and Processing, St. Mary's, PA, 16-18 October, (1989).

### III. CHARACTERIZATION METHODS

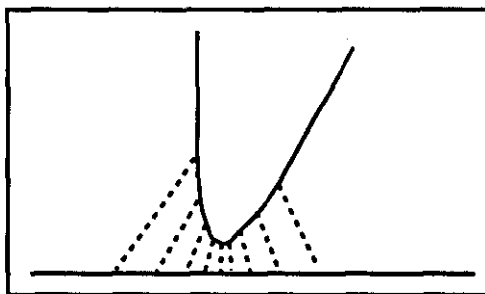
A critical component in the development of new materials, characterization takes many forms for the property of interest. If these techniques can be utilized to watch the evolution of nano-properties as a function of time, then mechanistic information may be obtained which could allow additional control of the properties resulting from such processes.

#### A. MICROSCOPY (Codes 4670, 6090)

A number of standard microscopic techniques are utilized routinely for characterization of nanometer-scale materials, and need not be elaborated upon here. These include Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Field-Ion Microscopy (FIM). Newer forms of microscopic examination are becoming of interest. Some comments regarding these follow.

##### 1. PROXIMAL PROBES (Codes 4600, 6030, 6100, 6300, 6800)

A remarkable revolution is currently taking place with the developing techniques involving scanning tunneling microscopy (STM), atomic force microscopy (AFM), and the many variations associated with these techniques. Atomic resolution was initially demonstrated with the tunneling tip by Binnig and Rohrer<sup>54</sup>, for which they were awarded the Nobel Prize. This technique was quickly picked up by the semiconductor community, which utilized it to examine surface reconstruction, defect formation, and various phenomena associated with semiconductor growth and behavior. A number of variations indicate its usefulness for characterization of magnetic effects at surfaces.



Subsequently there has developed a high level of interest in areas associated with molecular characterization (although this is still rudimentary and questionable in a number of cases reported) and the characterization of surface forces at the atomic and molecular level. This technique will probably lead to an understanding of energy loss mechanisms for friction at the nanometer level. The technique has been shown to give atomic resolution of surfaces as probed from solution, placing it in the category of being a surface probe able to characterize surfaces which are not restrained to high vacuum conditions (relatively few techniques are able to probe surfaces with atomic resolution at high pressures or in fluids). The dependence of the tunneling current with voltage provides, under ideal circumstances, information about the atomic species observed, thus enabling material identification at the atomic

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<sup>54</sup> G. Binnig and H. Rohrer, *Helv. Phys. Acta* 55, 726 (1982).

### III. CHARACTERIZATION METHODS

level for species on a surface. It is clearly useful for characterizing surface topography at the nanometer as well as the angstrom level of resolution.

Tunneling tip methods of characterizing surfaces are becoming common in all the fields associated with nanometer structures. Its appearance is mingling the interests of the various communities due to its broad applicability and the desire of researchers who have working instruments to apply their techniques to problems of interest. Characterization of nanocomposite materials for structural purposes has not embraced the tunneling tip methods as much as the other areas largely due to the fact that the crystal sizes making up samples are still characterized by other standard microscopic techniques.

A trend noted at the most recent international conference on tunneling techniques is that the field seems to be bifurcating into 1) force microscopy, 2) biologically interesting measurements, and 3) semiconductors and metals. Another observation offered is that the community utilizing these techniques is moving more in the direction of characterizing dynamic effects.

A "coulomb blockade" is a phenomenon in which the presence of a single electron so disturbs the field leading to conduction that the passage of additional electrons are inhibited. This takes place, for example, when a capacitor is so small that the voltage is significantly altered by the addition of a single electron. Electron flow through a conductor becomes correlated under these conditions, and "shot" noise is less than the traditional value for a given current. Tunneling studies are examining this effect.

It is possible to utilize a magnet at the tip of a tunneling probe, and to measure the current between magnetic domains and the magnetic tip. As the spin alignment between surface and tip changes, the tunneling current changes, thus providing angstrom-dimension resolution with these magnetic probes.

Tunneling tip techniques are providing new insight to electrochemical phenomena. The structure of surfaces modified by current or other chemical means has been examined under a number of conditions. The surface behavior depends on the solution composition, providing rich and complex problems to examine and understand.

Near field techniques for probing surface structure have undergone significant advances recently. R. Kopelman<sup>55</sup> at the University of Michigan has developed techniques using micropipettes which are able to produce inner diameters of less than 50 nm. Tiny molecular crystals are inserted in the tip of this micropipette. Light may be absorbed in a crystal in the form of excitons. This excited form of energy can migrate to the end of a small crystal, producing a nanometer-dimension source of light at the tip of the pipet. The spot size emerging from these devices is a

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<sup>55</sup> K. Lieberman, S. Harush, A. Lewis, and R. Kopelman, *Science* **247**, 59-60 (1990). A Light Source Smaller Than the Optical Wavelength.

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small fraction of a wavelength near the tip. Claims<sup>56</sup> (as yet undemonstrated) suggest hopes for molecular imaging with such probes. Other probes have utilized optical fiber probes at a surface to sense the evanescent wave of light trapped in an Attenuated Total Reflectance (ATR) experiment. By scanning the position of the fiber, the intensity of the light coupled to the fiber varies with position, producing an image of the surface. The limit of the resolution using this technique is a fraction of a wavelength of the light used.

#### NRL:

There is an NRL ARI examining forces between functional groups on molecules. This ARI entitled "Intermolecular & Surface Forces: Adhesion/Nanomechanics," focusses on intermolecular and surface forces contributing to adhesion and other dynamical interfacial processes. The utilization of this tool for micromechanical properties of materials has been reviewed recently<sup>57</sup>. It is leading to atomistic models for the mechanisms of adhesion, compression and fracture of surfaces<sup>58,59</sup>.

An NRL paper has recently appeared<sup>60</sup> which shows clearly aligned molecules of a nematic liquid crystal (4'-n-hexyl-4-cyanobiphenyl) on graphite. Atomic features of the molecule on the surface can be observed in the images obtained in this experiment.

The NRL Electronics Science and Technology Division is procuring equipment which will set up capabilities to utilize near field optical microscopy in the FY92 time frame. The instrument will be able to examine absorption and luminescence by species at a surface in the current configuration.

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<sup>56</sup> Chem. & Eng. News, p. 6, 8 January (1990). Technique generates ultrathin light beams.

<sup>57</sup> U. Landman, W. D. Luedtke, N. A. Burnham, and R. J. Colton, Atomistic Mechanisms and Dynamics of Adhesion, Nanoindentation, and Fracture, Science, **248**, 454-461 (1990).

<sup>58</sup> J. A. Harrison, D. W. Brenner, C. T. White, and R. J. Colton, Atomistic mechanisms of adhesion and compression of diamond surfaces, Thin Solid Films, **206**, 213-219 (1991).

<sup>59</sup> J. A. Harrison, C. T. White, R. J. Colton, and D. W. Brenner, Nanoscale Investigation of Indentation, Adhesion and Fracture of Diamond (111) Surfaces, Surf. Sci. Lett. (in press), (Jan. 1991).

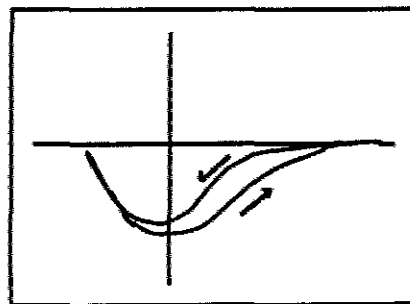
<sup>60</sup> S. L. Brandow, D. P. DiLella, R. J. Colton, and R. Shashidhar, Evidence of pronounced positional order at the graphite-liquid crystal interface of a bulk nematic material, J. Vac. Sci. Technol. **B 9** (2), 1115-1118 (1991).

### III. CHARACTERIZATION METHODS

Researchers in Code 6030 have attempted measurements involving the surface characterization of nearly amorphous materials such as quartz by using tunneling techniques and Atomic Force Microscopy (AFM). Results to this date have not shown atomic resolution even for crystalline quartz. In similar experiments, epitaxial diamond has been examined for etch pits produced in the production process. There are additional efforts to image protein molecules in solution with tunneling techniques.

Indentation techniques have traditionally been utilized to obtain the hardness of materials. With tunneling tip techniques, the penetration depth may be measured directly and dynamically. Energy loss can be obtained by analyzing the hysteresis curve for the experiment.

The magnitude of the indentation is so small that dislocations are not generated, so these experiments measure the hardness of the ideal material. NRL has introduced methods to probe the surface forces associated with a single film using these techniques<sup>61</sup>. A major question which is being asked today is: "What do these numbers really mean?"



By utilizing a tunneling tip near a surface as a photovoltaic probe, it is possible to examine the material several layers beneath the surface (penetration depth of the radiation). The technique utilizes suitably modulated and phase detected signals. NRL experiments have demonstrated images of GaAs/AlGaAs multilayer structures using this technique.

An ONT 6.2 program involves tunneling techniques to measure magnetic fields. A magnetometer can be designed in which a tunneling tip is used to measure the position of a torsion balance. In one version of this magnetometer, the deflection of a torsion bar which consists of a magnet changes with magnetic field. This technique has been shown to have a sensitivity of detecting changes of  $10^{-5}$  Gauss. A second magnetometer has been designed to measure the Lorentz force with a tunneling tip, measuring deflection in a wire through which current is passing. This effort is joint with the Jet Propulsion Laboratory (JPL).

Another 6.2 program at NRL is investigating the use of tunneling tip techniques to detect the presence of a single molecule which may be bound to an antigen. As such, it could possibly determine the presence of antibody-antigen pairs and represents a basis for a sensor detecting single molecule events for the adsorption of biologically active gases (a CB Defense sensor).

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<sup>61</sup> N. A. Burnham, D. D. Dominguez, R. L. Mowery, and R. J. Colton, Probing the Surface Forces of Monolayer Films with an Atomic-Force Microscope, Phys. Rev. Lett. **64**, 1931-1934 (1990).

### III. CHARACTERIZATION METHODS

There are ideas of designing experiments using tunneling tip techniques to examine clusters which have been formed or have been deposited on surfaces. These are just beginning at NRL, and may require some equipment modifications to locate tunneling tip equipment adjacent or in vacuum chambers.

#### B. DIFFRACTION TECHNIQUES

Standard X-Ray diffraction methods are still used to characterize grain or particle size, and to gain some information about the atoms which are found at the grain boundaries of multicrystalline materials.

Small angle neutron scattering is utilized on bulk samples to determine densities and grain boundary thicknesses. NIST has such facilities, but NRL does not make a great deal of use of this.

##### 1. NANODIMENSIONAL DIFFRACTION TECHNIQUES (Code 6030)

Code 6030 is in the process of developing nanodiffraction techniques which are able to gain structural information about amorphous (or nearly amorphous) materials. The approach is to image the atomic positions and electron densities of atoms in a very small sample, approximating a few angstroms in lateral dimensions, and some 25Å in the vertical dimension. The experimental portion of this program actually resides with a Scanning Transmission Electron Microscope (STEM) at Arizona State University. It has been modified to look at the diffracted electron beam rather than the image information usually associated with electron microscopy. The diffraction information is then examined as the beam is moved over fractional atomic distances in the sample. Electron densities of the regular crystal structures can be obtained for materials such as Si. An image with 1Å resolution has been obtained for Si using this instrument.

The big limitation of the current technique is to be able to collect the data efficiently so that instrumental adjustments can be made during an experimental run rather than through iterations involving a trip and computer interpretation of the data. New instrumentation which has more highly sophisticated controls is desired in order to improve the stability and image formation from these techniques. Cornell and Oak Ridge (using an annular detector without the diffraction feature at Arizona) are setting up new STEMs which can be utilized in this mode. The key element of this research effort is to really show the feasibility of gaining significant information about amorphous structures using this tool.

##### 2. SYNCHROTRON RADIATION

The synchrotron represents a major tool for diffraction (as well as for scattering and spectral absorption). NRL's synchrotron facility at Brookhaven, the National Synchrotron Light Source (NSLS) represents a significant investment which can provide characterization information. It is worth noting, in addition, that the Synchrotron Facility at Cornell (CHESS) is in the process of installing a 12-pole wiggler; when this is completed, in 1 to 1-1/2 years, the flux from this facility will



### III. CHARACTERIZATION METHODS

equal that being constructed at Brookhaven<sup>62</sup>. Additional synchrotron facilities are the Advanced Light Source, Berkeley, and the Advanced Photon Source, Argonne.

#### C. SCATTERING TECHNIQUES

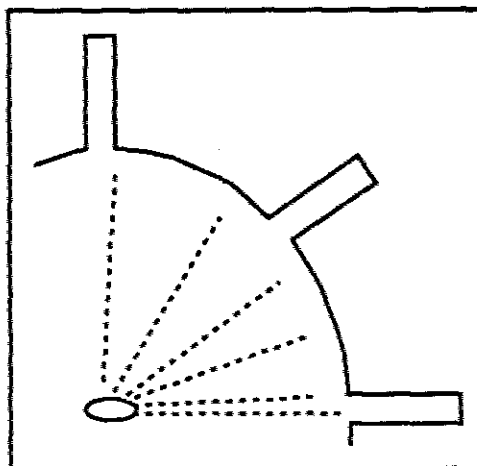
A number of the more standard scattering techniques are utilized as part of film growth and characterization. These include techniques such as Low Energy Electron Diffraction (LEED), Reflection High-Energy Electron Diffraction (RHEED), Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS), and X-ray Photoelectron Spectroscopy (XPS). Some description of additional variations will be given below.

##### 1. ANGLE-RESOLVED AUGER SCATTERING AND X-RAY PHOTOEMISSION (Code 6345)

A new NRL program in 1991 involves characterization of film structures involving the first 1-5 atomic layers using angle-resolved Auger scattering and X-Ray photoemission from these layers. This technique is relatively new and is being introduced at places such as UC Davis, U. of Washington, U. of Cincinnati, and NIST.

By examining the angular distribution of Auger electrons from ultra-thin films which are 1, 2, or 3 monolayers thick, a distinctly different scattering pattern can be observed. This gives important information relative to characterizing the local structure both in and out of the plane involving the top several layers of thin films. The surface topography relative to steps, islands, etc. can be readily discerned using this form of scattering. An example which has been examined at NRL is the growth of Fe on ZnSe (which forms in well-defined monolayers) and on GaAs (which forms in islands). A number of film properties are critically dependent on the surface topography. The mechanism of film growth can be determined with these techniques.

These techniques are selective to specific atomic sites (e.g., it can distinguish  $Ga^{++}$  from  $Ga^{+++}$ ). Newer techniques such as angle-resolved electron excitation processes are also being introduced as these scattering processes are being understood. Preparation of samples for these studies are typically done at NRL with MBE techniques, or by utilizing localized evaporation by electron beam heating of suitable metal samples.



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<sup>62</sup> Private communication, January, 1992.

### III. CHARACTERIZATION METHODS

The purchase of an angle-resolved Auger scattering and X-ray photoemission spectrometer at NRL is currently postponed due to cutbacks in budgets for FY92. When it is obtained, it will be placed in the NRL Epi-Center.

By resolving the electron spin of the scattered Auger electrons (or from Electron Energy Loss Spectra, EELS, for example) information can be extracted such as the sample magnetization or the magnetic domain structure. This represents a future endeavor to be exploited at NRL. Expertise in this type of scattering is currently at UC Irvine and Rice University.

A related technique involves the utilization of circularly-polarized photons from synchrotron radiation. Circularly polarized radiation is associated with specific selection rules, and creates spin-polarized holes in a solid material. Information related to the electronic structure of the material is obtained in this manner. Circularly polarized soft X-Rays are not readily available from synchrotrons since undulators typically produce plane-polarized radiation only. The National Synchrotron Light Source (NSLS) has some ability to do this kind of scattering currently (Bell Labs and IBM are entering this field). As the opportunities are recognized for this type of scattering there may be modifications to undulators to produce this kind of radiation. Facilities at the NSLS at Brookhaven are currently shared with Bell Laboratories for these experiments.

#### 2. BALLISTIC ELECTRON EMISSION MICROSCOPY (BEEM)

Electrons emitted from a semiconductor coated with a thin (100Å) metal layer on the surface can pass through the metal layer with little chance of collision. The spatial distribution of these electrons mirror the distribution from the semiconductor surface. The current in the semiconductor is measured as a function of a scanning tip forming a raster, giving 1-2 nm resolution. This technique is thus able to examine structural variations beneath the metal surface, and is a powerful technique for examining Schottky barriers and for quality control inspection of semiconductor devices. ONR-funded investigators have found that an image can be written beneath the metal surface with proximal probe techniques operating at somewhat higher voltages than those used to scan images. The mechanism for this is not presently well understood.

#### 3. SECONDARY ELECTRON MICROSCOPY WITH POLARIZATION ANALYSIS (SEMPA)

This technique utilizes a small focussed electron beam from an electron microscope. Secondary electrons are emitted which have a spin polarization associated with them. This technique can be utilized to probe magnetic structure in a surface. A desirable apparatus which has not yet been successfully constructed, and which has attracted considerable attention, would be one which emits spin polarized electrons and which could operate much in the mode of a scanning tunneling tip. A facility with these capabilities is located at NIST.

### III. CHARACTERIZATION METHODS

#### 4. EXAFS

The technique of utilizing Extended X-Ray Absorption Fine Structure (EXAFS) provides near neighbor information for specific scattering species. At distances of several angstroms, the order of a given environment can be determined with such an instrument. NRL's facility at Brookhaven is utilized for a number of projects involving this technique.

#### D. OPTICAL TECHNIQUES

##### 1. PHOTOREFLECTANCE

Photoreflective techniques provide a great deal of information about the band structure of semiconductors. NRL was a leader in utilizing interactive photoreflective techniques in which the influence of one beam on the reflectance of another is observed.

##### 2. PHOTOLUMINESCENCE

A very recent observation has been made by NRL concerning porous silicon. Porous silicon is a material with a fibrous structure in the nanodimensional region; it is found to luminesce red. The red color is higher in energy than the usual band structure for silicon, and the initial community reaction to this phenomenon was that the "blue shift" was due to quantum confinement. However, NRL observations have recently and conclusively shown that the red color is due to surface states involving hydrogen.

##### 3. OPTICAL SPECTROSCOPY

Since energy levels change when the wall dimensions become comparable to the wavelength of particles responsible for energy levels, spectroscopic techniques are responsible for a great deal of information related to the behavior of nanometer-sized particles.

A frequently pursued spectroscopic phenomenon in semiconductors is that of plasma excitation. This excitation involves a number of conduction electron oscillatory modes within confined structures. NRL has shown that spin density waves are out of phase with the usual electron density waves in certain zinc blende structures. These two waves are apparently coupled through the spin-orbit coupling mechanism.

##### 4. MOSSBAUER SPECTROSCOPY

This technique can be used to determine the local atomic environment for a specific atomic species. Occasional use of this technique is found at NRL.

### III. CHARACTERIZATION METHODS

#### 5. POSITRON LIFETIME SPECTROSCOPY

This technique is important for investigating the size of defects, being sensitive to crystal volume relative to crystal vacancies, voids, etc. This technique is not apparently used at NRL presently.

#### E. ELECTROCHEMICAL TECHNIQUES (Code 6322)

The electrochemical behavior of surfaces prepared by ion beam techniques relates directly to the corrosion characteristics of the materials. Utilizing the NRL ion implantation facility for the preparation of aluminum surface alloys, a model for the corrosion resistance of this metal with a variety of implanted metals has been generated. The model relates pit initiation of aluminum in a sodium chloride environment to the "pH of zero charge" of the oxide of the implanted material. The use of ion-implanted films for corrosion inhibition is also being studied at Oak Ridge and the Army Testing Laboratory in Massachusetts. Spire Corp. provides commercial ion implantation materials for various applications. The Japanese have recently published studies on the use of ion implantation to improve the corrosion resistance of steel.

#### F. SURFACE CHARACTERIZATION TECHNIQUES IN GENERAL

Techniques to characterize surfaces such as Auger microscopy, Secondary Ion Mass Spectrometry (SIMS), Rutherford Back Scatter (RBS), Raman scattering, etc. have been useful for a number of years in providing composition information about thin layers. These techniques should prove to be useful for numerous studies involving thin films or heterojunctions involved with nanomaterials which are small in a single dimension.

#### G. CHEMICAL CHARACTERIZATION

Catalytic activity is generally greatly enhanced with increasing surface dispersion. Smaller particle sizes inherently expose greater surface area per unit mass of catalyst. Further, catalytic activity can have some dependence upon particle size, particularly as the particles approach nanometer dimensions. This is apparently due to the change in electronic structure of the material due to confinement effects. This area offers some commercial interest, as exemplified by ongoing research at NRL on catalysts for fuel-cell reactions. Samples are prepared, for example, with platinum clusters having only about 200 atoms per cluster on a graphite surface. These samples are examined with EXAFS at NSLS. It is found that the platinum clusters appear to flatten out at high electrochemical potentials, indicating structural changes may be responsible for variations in catalytic activity associated with these samples.

## IV. PROPERTIES

A number of properties often are enhanced by reducing grain or fiber size, including the mechanical, thermal, electrical, and magnetic properties of ceramics, metals, and composites. When particulate size of a bulk material approaches tens of nanometers, a major fraction of the material is actually at the interface (or crystallite surface). The properties of this interface material is quite different than that of the bulk material, hence significant variations on the properties of the "composite" results. A major question relates to the actual properties of the grain boundary. Apparently the material between grain boundaries is amorphous. In most cases, these properties are unknown, compounding the difficulty of predicting bulk properties containing such small particles.

### A. SCALE LENGTHS

A number of phenomena exhibit phenomena characterized by critical lengths. These lengths are approaching the dimensions of the particle size, thus the following phenomena are likely to demonstrate different properties as particle dimensions approach nanometers:

Meissner coherence length	Superconductivity	1-1000 nm
Correlation length	conductivity	10-100 nm
Collision length (phonons)	conductivity	1-1000 nm
Materials Dislocations	mechanical strength	
Ferromagnetic domain walls	magnetism	~100 Å 10 nm
Ferroelectric domain walls	ferroelectric effects	10-100 Å 1-10 nm

### B. THEORETICAL INVESTIGATIONS

#### 1. TUNNELING IN QUANTUM DOTS (Code 6800)

The coupling behavior between three quantum dots has been examined theoretically at NRL with interesting predictions<sup>63</sup>. The quantum dots resemble artificial giant atoms with transitions predicted based on behavior analogous to transitions between atomic orbitals. Theoretical work suggests that the behavior of closely-coupled quantum dots can serve as a basis for logical operations (quantum-coupled logic).

#### 2. PHONONS (Code 6800)

The charge carrier relaxation time in a solid depends on the phonon structure of the medium through which these carriers migrate. The phonon structure is sensitive to the dimensions of a particular structure and to the uniformity of the structural walls, particularly when nanometer dimensions are achieved. NRL has

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<sup>63</sup> C. Y. Fong, L. A. Hemstreet, R. F. Gallup, J. S. Nelson, L. L. Chang, and L. L. Esaki, Tunneling in Quantum Dots (paper submitted 1992).

## IV. PROPERTIES

calculated electron scattering rates off polar optical phonons in quantum well<sup>64,65</sup> and wire<sup>66</sup> structures as a function of quantum well width. The effects of these phonon-electron interactions are manifested in optical spectra, particularly with absorption edge and exciton absorption spectra<sup>67,68</sup>. The effects of confinement appear to change the relaxation effects substantially, providing the potential for interesting new material properties.

### 3. TRANSPORT PHENOMENA IN DEVICES (Code 6800)

NRL theoretical developments in transport phenomena consist of solving the full Quantum Distribution-Function Transport Equation, which includes quantum tunneling and quantum interference effects, and all many-body effects<sup>69</sup>. In the Classical limit (Planck constant equated to zero), the equation reduces to the classical Boltzmann transport equation. Calculations using this theory have been used to simulate resonant tunneling devices with good agreement<sup>70</sup>. Phenomena such as bistability in resonant tunneling devices has been a subject of controversy in the literature recently. Application of the NRL approach appears to have not only simulated this behavior but has shown the origin of the phenomenon. This tool represents a powerful approach to simulating the transport behavior of nanostructures.

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<sup>64</sup> S. Rudin and T. L. Reinecke, Electron-LO-phonon scattering rates in semiconductor quantum wells, Phys. Rev. B, **41**, 7713-7717 (1990).

<sup>65</sup> P. A. Knipp and T. L. Reinecke, Coupling of electrons to interface phonons in semiconductor quantum wells, (paper submitted, 1992).

<sup>66</sup> P. A. Knipp and T. L. Reinecke, Interface phonons of quantum wires, (paper submitted 1991).

<sup>67</sup> S. Rudin and T. L. Reinecke, Phonon-assisted optical absorption by excitons in semiconductor quantum well, Phys. Rev. B **39**, 8488-8493 (1989-II).

<sup>68</sup> I. C. da Cunha Lima and T. L. Reinecke, Infrared Absorption Due to Electron-Lattice Vibration Scattering in GaAlAs/GaAs Quantum Wells, (paper submitted, 1992).

<sup>69</sup> F. A. Buot and K. L. Jensen, Lattice Weyl-Wigner formulation of exact many-body quantum-transport theory and applications to novel solid-state quantum-based devices, Phys. Rev. B, **42**, 9429-9457 (1990).

<sup>70</sup> K. L. Jensen and F. A. Buot, Numerical Simulation of Intrinsic Bistability and High-Frequency Current Oscillations in Resonant Tunneling Structures, Phys. Rev. Lett. **66**, 1078-1081 (1991).

## IV. PROPERTIES

A novel idea gaining interest at NRL is the possibility of utilizing narrow-gap semiconductors for interesting transport properties in semiconducting devices. The interference effects in resonant tunneling devices has been recognized for several years. Lateral surface superlattice field effect transistors are shown to demonstrate resonant behavior, but primarily at low temperatures. By utilizing low band gap semiconductors having very low effective masses (such as HgTe/CdTe, with  $m^* \sim .001$ ) these resonant effects should be evident at higher temperatures (room temperature). This provides a way to utilize the advantages of resonant structures in horizontal devices, which are easier to manufacture.

### 4. ELECTRONIC PROPERTIES (Code 4600)

Advanced computational models such as so-called gradient corrections to the Local Density Approximation are increasingly powerful tools for calculating the electronic properties of clusters and other small segments of matter. Large-scale parallel computers will enhance the computational capabilities of these tools further. Transport and thermodynamic properties can be estimated with sufficient accuracy to be of use to experimentalists working with these properties.

## C. ELECTRONIC PROPERTIES

### 1. TRANSPORT PROPERTIES (Code 6800)

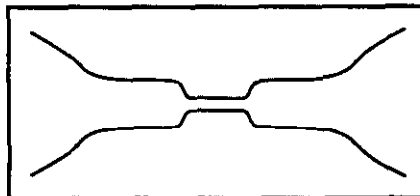
Of all the properties involving nanometer-sized fragments of matter, the transport properties represents the one which is probably of most interest in terms of the economic impact likely for the country. The electronics and computer industries are based on the transport behavior of carriers in semiconductors. The MOSFET appears to be the dominant technology for the microcomputer industry today. Variations of this structure as well as alternative forms of switching are being examined for device behavior. The volume of reference material related to this subject is so large that the following comments can only touch on the broadest points related to this field, rich in the variations and permutations which have been pursued.

Nanometer dimensions were first achieved for mass production by growth techniques in the production of heterojunction materials. The advantages achieved by such materials include 1) variable bandgap, hence the ability to engineer material properties with physical dimensions; and 2) high mobility of carriers in lateral transport. The development of MBE and Atomic Layer Epitaxy (ALE) for production of such materials is well recognized. Problems in this field include gaining a high degree of quality control over the dimensions and layer definition of the materials obtained.

Rolf Landauer (nearly 20 years ago) stated: "... electronic transport is fundamentally and simply described by summing up the conductances of all possible channels, each having a well defined quantum mechanical transmission coefficient. A consequence of this formalism is that conductance will be quantized, in units of

#### IV. PROPERTIES

$e^2/h$  per spin, in the limit of a few ballistic electron channels."<sup>6</sup> It is found that the conductance,  $G$ , across a constriction (illustrated in accompanying figure) varies in a step-like fashion, with plateaus at  $G = 2n e^2/h$ , for integral  $n$ .<sup>6</sup> This behavior has been observed by a number of researchers (see for example work by Timp and Howard<sup>71</sup>). The relationship is simply an expression of the uncertainty relationship, applied to electrons in guided wave structures<sup>3</sup>.



Carrying the limit of size to that of molecular dimensions, some consideration has been given to the conductivity which may be observed for that of a single molecule<sup>72</sup>. With the appearance of STM and nanolithography techniques, it may be possible to realize such an experiment. A conclusion of the referenced article is that an order of magnitude conductance may be expected to be around  $10\text{ G}\Omega$ . The current which would be expected would be about  $10\text{ pA}$  for a voltage of  $10\text{ mV}$ .

Reductions to below about  $0.2$  micrometers will introduce significant fundamental problems<sup>14</sup>. These include material breakdown at the voltages used by a functioning device; the "wiring crisis," which suggests that at such small dimensions it will not be possible to construct a lead to each transistor due to the impossibly crowded conditions; resistance and capacitance effects become increasingly more difficult to handle at these smaller dimensions; hot electron injection into thin gate oxides at the drain alter device characteristics; and edge definition, which typically is irregular to  $0.1$  microns, limits the uniformity of devices defined at these smaller dimensions. It is clear that there are a large number of challenges associated with a simple extension of techniques used above  $0.1$  microns. Innovative solutions will be needed for many different aspects of this challenge.

Given that devices having  $0.2$ - $0.5$  micron lateral dimensions have been made by parallel production techniques and are expected to be commercially available over the next several years, attention in this document should be given to those phenomena which exhibit alternative behavior to what is now conventionally utilized or projected for commercial introduction. Behavior of structures having these small dimensions may be categorized into 1) resonant tunnelling devices, 2) ballistic electron transport, and 3) quantum interference devices.

##### **a. Resonant tunneling devices**

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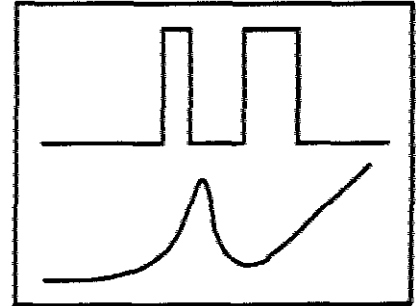
<sup>71</sup> G. L. Timp and R. E. Howard, Quantum Mechanical Aspects of Transport in Nanoelectronics, Proc. IEEE 79, 1188-1207 (1991).

<sup>72</sup> C. Joachim, New J. Chem. 15, 223-229 (1991). The Conductance of a Single Molecule.



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A Renaissance in vertical electronic transport through multilayer heterostructures was introduced with the demonstration of large quantum tunneling effects in resonant tunneling structures<sup>7 3</sup>. The significance of these experiments was the realization that artificially-structured quantum states could show nonclassical electronic transport.



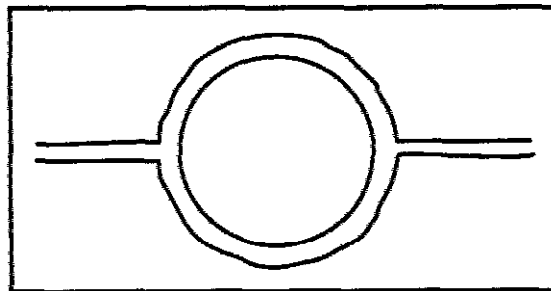
Resonant tunneling of electrons through quantum wells produce negative differential resistance as the wave-barrier interactions reinforce and interfere at various voltages. Self-oscillating structures are able to produce frequencies of several hundreds of GHz, suggesting considerable impact of these structures for microwave oscillators and devices.

##### **b. Ballistic electron transport**

If the coherence length (closely associated with the mean free path) of electron carriers is greater than the dimensions of a given device, then transport involves a minimal number of collisions as they migrate through the material. In GaAs, for example, the mean free path of electrons is estimated to be on the order of a few hundred nanometers at low temperatures in pure material. Electrons having sufficient energy to surmount a barrier have greater speed than the average of the ensemble before barrier penetration. Devices utilizing primarily this effect have demonstrated ballistic transport along with a variety of properties associated with this type of transport. Such devices show interference effects, to be discussed next.

##### **c. Quantum interference devices**

As the size of semiconductor devices becomes smaller than the mean free path of the carriers, electron phase information is retained over the size of the device. Interference effects are important to recognize in such cases. Major modifications in the transport properties of ballistic electrons propagating in two parallel channels is observed by adjusting the relative phase in each channel. The optical analog is that of the Mach-Zender interferometer.



The resulting Aharonov-Bohm oscillations

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<sup>73</sup> T. C. L. G. Sollner, W. D. Goodhue, P. E. Tannenwald, C. D. Parker, and D. D. Peck, Appl. Phys. Lett. **43**, 588 (1983).

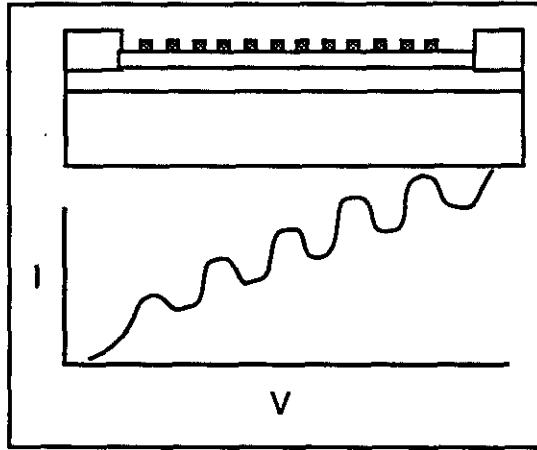
#### IV. PROPERTIES

have been observed in small ring structures<sup>74</sup>. A phase shift may be induced through electric or magnetic field perturbations. Substantial consideration is being given to variations of such devices. They are predicted to have high transconductance and low power dissipation, and may possibly provide picosecond switching capabilities. A comprehensive perspective is presented in the following statement<sup>75</sup>:

"...the real power and utility of quantum devices may ultimately lie not in the implementation of conventional transistors having a source, a drain and a gate (where the low current capability is a major concern) but in the implementation of programmable multi-terminal quantum networks that could lead to radically new concepts for information processing with electronic devices."

##### **d. Field-effect-controlled nanostructures**

A number of innovative quantum interference devices have been examined experimentally which utilize field depletion regions of heterojunctions to define nanodimensional structures<sup>76</sup>. A number of variations have been fabricated to examine conduction and interference phenomena at nanometer dimensions. These include MODFETs, grating-gate lateral surface superlattices (LSSLs), planar-resonant-tunneling field-effect transistors (PRESTFETs), and arrays of quantum dots (QDs). By patterning the overlayer Schottky contacts parallel or perpendicular to the direction of carrier flow, or by patterning these contacts in a grid pattern as opposed to "wires," a great variety of phenomena can be observed.



Interference effects observed correspond closely to those expected based on prior knowledge of these devices. Multiple extrema in the current-voltage relationships suggest the possibility of multi-level logical elements, now that such devices can be fabricated and effectively characterized. Further variations involving such devices

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<sup>74</sup> R. A. Webb, S. Washburn, C. P. Umbach, and R. B. Laibowitz, *Phys. Rev. Lett.* **54**, 2696 (1985).

<sup>75</sup> S. Datta, *Quantum Interference Devices*, in F. Capasso, *Physics of Quantum Electron Devices*, Springer-Verlag, NY (1990).

<sup>76</sup> K. E. Ismail, P. F. Bagwell, T. P. Orlando, D. A. Antoniadis, and H. I. Smith, *Quantum Phenomena in Field-Effect-Controlled Semiconductor Nanostructures*, *Proc. IEEE* **79**, 1106-1116 (1991).

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utilize laterally-confined tunneling junctions<sup>77,78</sup>. An alternative name of Resonant Tunneling Field-Effect Transistor (RTFET) has been dubbed for lateral quantum wires on a gate.

An additional physical phenomenon which becomes evident in such small structures due to wave delocalization effects is that of fluctuations in voltage which are observed at points adjacent to conductors. Statistical fluctuations in fields associated with the passage of a finite number of carriers are transmitted nanometers along connections adjacent to the conducting path.

#### NRL:

NRL has made a great number of measurements characterizing the transport properties of semiconducting materials. Mention here is of the several more recent measurements characterizing those properties associated with material and device behavior at very small dimensions.

NRL experiments have demonstrated the existence of nanometer-scale conduction channels generated by the strain fields of crystalline dislocations passing through semiconductor tunnel barriers.

Under illumination, the electrical resistance of these channels show discrete changes in time. These discrete changes in resistance of the channel are caused by the change in charge state of single charge traps which modulate the current flow through the channel.<sup>79</sup> Each discrete change in resistance corresponds to the capture or subsequent release of a single photogenerated charge by a single charge trap. This effect permits the detailed optical probing of the charge kinetics of a single trap. In addition, this phenomenon can be

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<sup>77</sup> J. H. Luscombe, J. N. Randall, and A. M. Bouchard, Resonant Tunneling Quantum-Dot Diodes: Physics, Limitations, and Technological Prospects, Proc. IEEE 79, 1117-1130 (1991).

<sup>78</sup> S. Y. Chou, D. R. Allee, A. R. F. Pease, and J. S. Harris, Jr., Lateral Resonant Tunneling Transistors Employing Field-Induced Quantum Wells and Barriers, Proc. IEEE 79, 1131-1139 (1991).

<sup>79</sup> P. M. Campbell, E. S. Snow, W. J. Moore, O. J. Glembocki, and S. W. Kirchoefer, Light-Activated Telegraph Noise in AlGaAs Tunnel Barriers: Optical Probing of a Single Defect, Phys. Rev. Lett. 67, 1330-1333 (1991).

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used as an extraordinarily sensitive means of detecting single photons.<sup>80</sup> Each jump into the low-resistance state corresponds to the absorption of a single photon. Since the change in resistance is mediated by a single charge trap, there are no competing noise mechanisms. This results in background dark counts which are unmeasurably low (corresponding to fluxes of less than one photon per hour), which is far better than current state of the art CCD or photomultiplier technologies. Further



efforts are continuing to see if such naturally occurring nanostructures can be fabricated in a controlled fashion to produce a new class of optical devices based on the action of single charge traps.

##### 2. SUPERCONDUCTING PROPERTIES (Codes 6340, 6325)

The two characteristic lengths of a superconductor are the coherence length,  $\xi$ , and magnetic penetration depth,  $\lambda$ . Since these lengths are quite short,  $\xi \sim 15\text{\AA}$  in high  $T_c$  superconductors (HTS) and  $10^2 - 10^3\text{\AA}$  in low  $T_c$  superconductors (LTS), and  $\lambda \sim 10^3\text{\AA}$  in both HTS and LTS, a cryogenic STM is ideal for the study of these materials. Such a system is in the process of being shipped to NRL for the purpose of studying both the HTS and LTS.

When a normal metal or semiconductor is in intimate contact with a superconductor and the superconducting electron pairs "leak" into them. This phenomenon is called the "proximity effect." These "leaked" superconducting pairs have a  $\xi$  which is a characteristic of the proximity material and will be probed at NRL by tunnelling spectroscopy with the STM. An interesting variation to be examined at NRL is the replacement of the normal metal with a semiconductor, to observe the behavior within the semiconductor under these conditions. This phenomenon requires clean interfaces, especially for the HTS, and is technologically important for superconducting electronic devices and contacts.

A magnetic field penetrates a type II superconductor in the form of vortices which consist of normal, magnetic cores with radii  $\xi$ , surrounded by a superconducting region penetrated by a magnetic field whose magnitude decreases exponentially with a characteristic length  $\lambda$  from the core (effectively  $1500\text{\AA}$  in yttrium barium copper oxide). Studies of these features are important for resolving controversies concerning the nature of flux dynamics and pinning properties of the HTS. The details of this structure can be studied using the STM mentioned above, with expected resolution of  $10-100\text{\AA}$ . These experiments are essential for understanding and exploiting these materials' high current and high magnetic field properties.

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<sup>80</sup> E. S. Snow, P. M. Campbell, O. J. Glembocki, W. J. Moore, and S. W. Kirchoefer, An Extremely Sensitive GaAs/AlGaAs Solid-State Photon Counter, Appl. Phys. Lett. 56, 117-119 (1990).

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In order to prevent dissipation in the superconductor in the presence of large transport currents, the vortices must be prevented from moving, i.e., they must be pinned on defects that are on the scale of the coherence length. NRL will attempt to introduce some nanosize particles by making a composite material consisting of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the superconducting phase, as the material is interspersed with a nanosize dispersion of  $\text{Y}_2\text{BaCuO}_5$  which is chemically compatible with the superconductor but is an insulator.

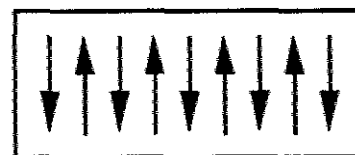
The change in superconducting properties as a function of grain size is also under investigation at NRL. Gleiter (see Table I) showed that the critical temperature of aluminum increased from a value of 1.2K to 3.2K as the crystalline size is reduced to nanometer dimensions. Theoretical attempts are underway at predicting the critical current in nanocrystalline materials. An oscillatory behavior is predicted as a function of  $1/d$ , where  $d$  is the particle diameter (assuming a monodisperse sample). Peaks in critical currents are predicted in nanocrystalline superconducting materials.

#### D. MAGNETIC PROPERTIES (Codes 6090, 6340)

Nanodimensional magnetic structures are important from the point of view of 1) thin films which make up magnetic layers, and 2) magnetic domains which, under proper conditions, can form memory devices in very small dimensions. Also, magnetic structure can be probed by using a spin-polarized tunneling tip to study the behavior of magnetic domain walls.

Rare earth transition metal multilayer films have been produced at Phillips Laboratories, Germany, and measured at NRL which have giant anisotropies and which form "perfectly homogeneous" materials down to the 8 - 10 Å dimension. The materials are prepared with alternating layers of, e.g., Fe and Tb at 4 - 5 Å intervals. The importance of this material is that it could be useful as a recording material at room temperature (previously prepared materials exhibited such behavior only at low temperatures). Such highly anisotropic materials have very narrow domain wall widths (as small as a single atom). In fact, the question of what is a domain wall is an interesting question associated with such materials. A new facility is being introduced at NRL for ultra-high vacuum work for sputtering and Molecular Beam Epitaxy (MBE) which will allow preparation of these films at NRL. Another program involves Extended X-Ray Absorption Fine Structure (EXAFS) on amorphous Fe/Tb films. The origin of the anisotropy perpendicular to the film is of interest in these studies; this question may be solved with the newer tools being applied to it.

A new discovery by Julich (KFA, Germany) has shown that successive 50Å layers of iron separated by 10-30Å of chromium shows antiferromagnetic alignment of the magnetism in the iron layers. The coupling mechanism appears to be the exchange integral passing through the chromium layer. This sign of the exchange coupling oscillates as the thickness of the Cr layer changes, similar to what one expects from classical coupling effects. However the characteristic length



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scale is a factor of ten larger than what would be expected from ordinary exchange integral considerations. The mechanism for this phenomenon is under intense scrutiny in the community. Associated with this unusual antiferromagnetic coupling is a 50% change in resistivity (discovered in Orsay, France) with applied magnetic field. Commercial recording heads operate on a magnetoresistive effect which amounts to a 1-2% change in resistance. Since the speed of such a memory is proportional to the square of the relative resistance change, this phenomenon represents an effect which conceivably has considerable commercial opportunity, and is attracting a great deal of attention. It could possibly lead to nonvolatile memory components which have speeds comparable to or greater than current semiconductor memories. Applications for high value platforms such as satellites could be very attractive.

Magnetic semiconductors have been made in unusual circumstances. Materials such as ZnSe can be doped with 10-20% Fe, Mn, or Co in alternating superlattice structures (similar to GaAs/AlGaAs) and show a strong spin polarization in the layers due to the presence of the magnetic atoms introduced. The unusual property of these materials is that the g-value is on the order of 200 (as opposed to the normal value of 2 for the free electron)! These materials have been used to grow spin superlattice structures, and demonstrate that carrier spin may be used as a fourth degree of freedom, completely complementary to the three spatial degrees of freedom.

The magnetic equivalent of an FET is under examination at NRL. NRL is fabricating iron patterns on GaAs, filling in active regions with dilute semiconducting materials (such as ZnSe/ZnCoSe). Devices which are sensitive to magnetic fields in the same manner as an FET is to electric voltages are anticipated. It is hoped that optical Faraday isolator switches may be fabricated. Construction of non-reciprocal devices for optical fibers and integrated optics appears to have a high priority at the present time. Scattering effects in the optical region make this a requirement which is just as severe as that which introduced these devices in microwave equipment decades ago.

Spin injection represents an idealistic goal with significant ramifications. The spin polarization of electrons in metallic iron amounts to approximately 23% (more spin up than spin down). If electrons from iron are injected into a semiconductor which is particularly sensitive to magnetic fields (such as the dilute semiconductors mentioned above), the band gap can be significantly altered by the resulting magnetic field of the polarized electrons. Effectively, a 2 KGauss field can be introduced by this method by simply a few milliamps of current. It is possible to envision controlled magneto-optical effects which such techniques. NRL has a patent on this idea.

The magnetic properties of granular magnetic materials is being investigated in conjunction with the metallized tubules mentioned in the Fabrication/Self-Assembly section of this document. The magnetic coercivity of nickel-coated tubules is a strong function of the orientation of the tubules as well as the nature of the coating. Characterizing these materials with microscopic examinations, electron diffraction/imaging, and magnetic measurements is continuing. A potential

#### IV. PROPERTIES

application relates to the use of such materials as electrostatic screening agents to reduce cross talk in stripline microwave components.

##### E. OPTICAL PROPERTIES (Code 6500)

Nanostructures are important for their optical properties in two fundamental areas: 1) sources of radiation, and 2) for detectors. Quantum wires and dots have a potential for enhancing nonlinear optical phenomena and for providing active optical gain media with higher gain coefficients than for homogeneous materials. Energy level spectroscopy on small two-dimensional dots is taking place (much as with atoms) to characterize the band structures obtained by confinement. The manner in which these quantum features couple with one another in closely-spaced arrays is an area of interest being pursued.

New lasers have become commercially available from heterojunction structures. This is perhaps one of the first commercially realizable products of R&D in the entire area of nanoscience/technology.

Optical detectors for long wavelength IR have been made from GaAs nanostructures, but these devices must compete with detectors utilizing II-VI materials. They are currently 1 - 2 orders of magnitude less competitive, however they are being investigated for improvements. Bell Laboratories and Texas Instruments are particularly involved with such studies.

##### NRL:

A number of magneto-optical and quantum Hall studies have been conducted on superlattice structures<sup>81</sup>. This work has lead to subsequent interests in nonlinear optical properties for protection of optical sensors. Nonlinear optical properties are substantially influenced by certain nano-dimensional structures. For example, selected semiconducting layered materials such as InAs-AlSb-GaSb and BiSb-CdTe are being examined in Code 6550 for their nonlinear behavior. A desired objective is to create devices which would switch from transmission to reflection at a selected power threshold. While several nonlinear material systems are potentially able to do this, certain material limitations need to be overcome to make practical devices. Analyses have been made which indicate that, for most approaches considered<sup>82</sup>, the parameter  $n_2/(\alpha\tau)$  is an applicable performance parameter, where  $n_2$  is the third-order nonlinear index of refraction,  $\alpha$  is the material absorption coefficient, and  $\tau$  is the lifetime for recovery of the material. At some wavelengths, the operable parameter is more simply  $n_2/\alpha$ .

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<sup>81</sup> J. R. Meyer, R. J. Wagner, F. J. Bartoli, C. A. Hoffman, M. Dobrowolska, T. Wojtowicz, J. K. Furdyna, and L. R. Ram-Mohan, Magneto-optical properties of HgTe - CdTe superlattices, Phys. Rev. B, **42**, 9050-9062 (1990).

<sup>82</sup> Analysis by T. Campillo, Code 6500.

#### IV. PROPERTIES

One group in Code 6500 is concerned with utilizing total internal reflection at a threshold of high power levels for this effect. Layered materials involving, say, 200 atomic layers each of the semiconductors mentioned in the previous paragraph show considerable promise. "Type II" superlattices involve semiconductors in which the overlap between electron and hole carriers is minimized by concentrating each in the two different layers. Carrier lifetime is enhanced through such minimization of overlap. By further modifying the layered structure beyond those variations which have been first tried, increased values of  $n_2$  with reduced values of  $\alpha$  are anticipated. This program is relatively new (beginning in October 1991) and is rich in the fundamental physics which needs to be explored.

Quantum dots have been the subject of a number of investigations country-wide, however frustration has been expressed over the difficulty of obtaining easily characterized and uniform material. Recent efforts in Code 6500 have lead to a technique for producing 100 nm (or even 10 nm, thought possible) holes, regularly spaced, in glass. This material can be used as a template in which materials of interest may be placed, providing a flexible way to fabricate well defined quantum dots and wires in an otherwise optically transparent matrix. This technique should be generally useful for a number of studies on reduced dimensionality materials. Cooperative efforts involving Code 6100 (for synthetic approaches to filling the holes) to Code 6800 (for materials of interest for electronic applications and measurements) are developing here. The holes in these materials are regularly spaced, which is significant due to the cooperative phenomena which can take place affecting lifetime properties in a regularly spaced array.

Prior to this technique, the efforts in Code 6500 have stressed the fabrication and study of nonlinear optical properties of quantum dots in composites. CuCl/glass composites with dot radii from 20-40Å have been made and shown to have an extremely large nonlinearity. GaAs dots with radii from 15-25Å have been fabricated in vycor glass and plastic hosts. These samples have shown 200-300 nm blue shifts for the GaAs band structure due to confinement. Additional composites have been prepared using the metal atom reactor technique. Metal and semiconductor clusters in a chemically active polymer host such as poly-4-BCMU have shown greatly enhanced non-linear optical properties. Samples containing 7% gold without aggregation have demonstrated a non-resonant third-order optical susceptibility coefficient enhancement of 200 relative to poly-4-BCMU.

#### E. MECHANICAL PROPERTIES (CODE 6300)

Materials with nanocrystalline grain sizes typically show reduced density, increased thermal expansion, specific heat, and extremely high diffusion rates. Because of the extremely small grain sizes, up to 50% of the atoms can be located within the grain boundaries.

Sintered powders made with fine powders have increased density and uniformity, reduced shrinkage on firing, and reduced need for subsequent processing. A look at the properties of nanocrystalline metals as compared with their



#### IV. PROPERTIES

crystalline counterparts is given in Table I. Note that, for the limited sample size given here, nanocrystalline materials have higher thermal expansion coefficients, lower densities, lower elastic moduli, higher fracture stress, and a lower activation energy for diffusion. This suggests that such materials could give stronger materials at room temperature, but due to the lower activation energy for diffusion, higher temperature applications may be somewhat limited.

Table I  
Properties of Nanocrystalline Metals compared with their Crystalline and Glassy Counterparts<sup>83</sup>

<u>PROPERTY</u>	<u>MATERIAL</u>	<u>CRYSTAL</u>	<u>GLASS</u>	<u>NANOCRYSTAL</u>
Thermal expansion ( $10^{-6}/K$ )	Cu	16	18	31
Specific heat at 295K (J/gK)	Pd	0.24	-	0.37
Density (g/cm <sup>3</sup> )	Fe	7.9	7.5	6
Elastic moduli (GPa)				
Young's modulus	Pd	123	-	88
Shear modulus	Pd	43	-	32
Saturation magnetiz'n at 4 K (emu/g)	Fe	222	215	130
Susceptibility ( $10^{-6}$ emu/Oe g)	Sb	-1	-0.03	20
Fracture stress (Kp/mm <sup>2</sup> )	Fe/1.8%8	50	-	600
Superconducting T <sub>c</sub> (K)	Al	1.2	-	3.2
Activation energy for diffusion (eV)	Ag in Cu	2.0	-	0.64
	Cu in Cu	2.04	-	0.64
Debye temperature (K)	Fe	467	-	345

The desirable aspects of materials having sub-micron grain sizes are accompanied by additional features which mitigate some of the advantages of these materials. In particular, small grain sizes also enhance 1) atomic diffusion between grains and 2) dislocation mobility. The consequent behavior is one of enhanced rate of grain growth (Ostwald ripening) and enhanced creep or ductility. These can be desirable for enhanced formability, but undesirable from the point of view of maintaining many of the enhanced properties at high temperatures.

##### 1. STRENGTH, TOUGHNESS, MODULUS, ETC.

The Hall-Petch (H-P) relationship has been recognized for years as an important aspect of materials hardness. As particle size is decreased, yield strength seems to increase. However, Gleiter<sup>84</sup> has apparently shown that particle sizes which

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<sup>83</sup> C. Suryanarayana and F. H. Froes, Nanocrystalline Metals: A Review, Physical Chemistry of Powder Metals Production and Processing, St. Mary's, PA, 16-18 October, (1989).

<sup>84</sup> Scripta Metallurgica 23, 1679-1684 (1989).

#### IV. PROPERTIES

are several orders of magnitude smaller than the usual 10 micron grain sizes, although substantially stronger, show the reverse behavior (smaller size is correlated with decreasing yield strength). The basic reason for the H-P relationship seems to be associated with the build-up of dislocations at a grain boundary before material failure. Larger particle sizes can contain a greater number of dislocations, thus producing a higher number of dislocations localized at one place when under strain. Failure takes place more readily due to this higher concentration. Smaller particle sizes have fewer dislocations in them, hence less build-up of them at a grain boundary. However, when the particle size is so small that this build-up of dislocations cannot take place (less than one dislocation per grain), alternative mechanisms begin to be important.

The quantitative relationship is:

$$\text{Yield Strength} \propto 1/\sqrt{d}$$

where  $d$  is the particle diameter. The constraint which involves diffusion effects (and particle size growth through Ostwald ripening) imposes further limitations, as discussed in the previous paragraph. It is a valid relationship only if the composite consists of immiscible components, which helps to limit grain growth. Further, the yield strength of a composite is generally accepted to be the weighted average of the yield strength of the various components, proportional to the volume fraction of each. However, the properties of nanometer-sized particles is such that strengths greater than that of either component is possible, due to the fact that the composite property consists of such a large fraction of interfacial material. Thus, unexpected properties are expected when working with these materials. The extent to which these basic relationships are followed or not is unknown for nanocrystalline materials.

NRL has an ARI in this field which is almost completed. Materials which are being investigated at present include niobium particles in a copper matrix (with a small amount of nickel). Some increased strength has been indicated, but the unequivocal demonstration of this has been difficult to achieve. Samples have indicated sensitivity to impurities. Alternative methods of preparing more highly controlled materials is being pursued at present.

In addition to simply working with smaller particle sizes in a composite, some recent work by Hilliard suggested that metallic multilayers having some 20Å distance between them exhibit stiffness modulus several times that of the bulk value of either component. The reason for this was ostensibly due to dislocation pinning along with the fact that the majority of the material was interfacial, which presumably has different properties. This attracted a great deal of attention and disagreement in the materials community. Today the community consensus appears to be moving in the direction that there may be a 30-40% enhancement, but experimental difficulties probably account for the larger part of the enhanced modulus reported. Difficulties such as thin layers of oxide formation due to sample handling appear to be significant sources of error.

## **IV. PROPERTIES**

The commercial value of high strength materials made from nanometer-sized particles is an important driving factor. Some interesting speculations have been offered<sup>85</sup>:

"Consolidates made to date from nanometer scale metallic particles have not yet been shown to exhibit any properties that would make them worth their high production cost, and they may well remain laboratory curiosities for some time to come. On the other hand, an economic source of ceramic particles of nanometer sizes could make possible the production of formable ceramics with the improved properties inherent to flaw free materials. Another area of high potential for nanometer size particles is in the fabrication of dispersion strengthened metals."

### **2. CREEP**

The motion of grain boundaries leads to creep in materials. This is greatly enhanced with smaller grain sizes, and is a significant factor for grain sizes which are sub-micron in dimensions. One aspect of this motion is the introduction of creep, an irreversible deformation which is undesirable under almost any circumstances. Many of the desirable aspects of nanocrystalline materials could be mitigated by creep properties at higher temperatures. This aspect of nanocrystalline materials behavior must be carefully considered in the design of superior strength materials anticipated.

### **3. SUPERPLASTICITY (FORMABILITY)**

Another aspect of grain boundary motion is ductility, a highly desirable property for materials strength and formability. The undesirable aspects of grain boundary motion leading to creep are desirable if utilized in the processing of metals, alloys, and ceramics for structures.

The increased ductility of fine-grained materials leads to a phenomenon known as superplasticity, in which a tensile specimen may be elongated by factors of 10 or 100 before breakage. This property could lead to significant cost savings in forming structures of high performance materials. Currently many high performance materials are made with costly machining processes. If they could be molded, significant cost savings could be achieved.

The phenomenon of superplasticity has been recognized for years, however such materials have been limited in their application due to the difficulties of preparing them. NRL has a new start in the Materials Processes Task Area which will explore methods of specialized powders for composite precursors. A key to making this process useful is to gain deformability at high enough temperatures without the appearance of significant grain growth. This means controlling the stable submicron

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<sup>85</sup> J. D. Ayers, Fine Particles, Elliott Symposium Proceedings, pg. 273 (1990).

#### IV. PROPERTIES

grain sizes. This represents a carefully designed balance between the inherent limitations of thermodynamic equilibrium and kinetics.

An example of superplastic materials is made with the alloy mixture  $Ti_3Al/TiAl$ . This has been made by Martin Marietta, and the superior strength properties measured. Mechanical components made from this material are approximately 1/3rd the weight of Inconel-718. NRL's role in this has been to characterize the properties of these materials. At present, the preparation of this material is more expensive than standard techniques with more conventional materials. If a hot deformation technique utilizing superplasticity could be introduced, it would represent a significant cost savings. Alternative preparation and processing procedures could lead to advantages; however, a scientific base is required to point the way to such superior processes.

The advantages of superplasticity of sub-micron grain sizes in materials has been recognized for years. A world-wide expert on this subject is Professor O. Sherby at Stanford, who has been supported by ONR for 25 years. The NRL approach of hot pressing superplastic powder samples, however, represents a unique approach which has not been attempted elsewhere.

It is also apparently true that very small ceramic particles gives rise to ceramics which are ductile. This work has been carried out at Rutgers University. It is stimulating to imagine the possibility of preparing superplastic high-temperature superconducting materials. Limitations on current-carrying capacity of such a material may be present due to the high volume fraction of grain boundaries. One of the principle problems of making the high temperature superconductors commercially important has been the brittleness of the prepared wires and other items formed. This, however, is presently a gleam in the eye of researchers.

## V. COMPONENTS AND DEVICES

### A. ELECTRONIC DEVICES (Code 6800)

The variety of devices which evolve from the semiconductor world appears to be almost infinite. It is not possible to outline the great number of devices and effects associated with these phenomena. A list of some of the types of devices, replete with the acronyms, includes:

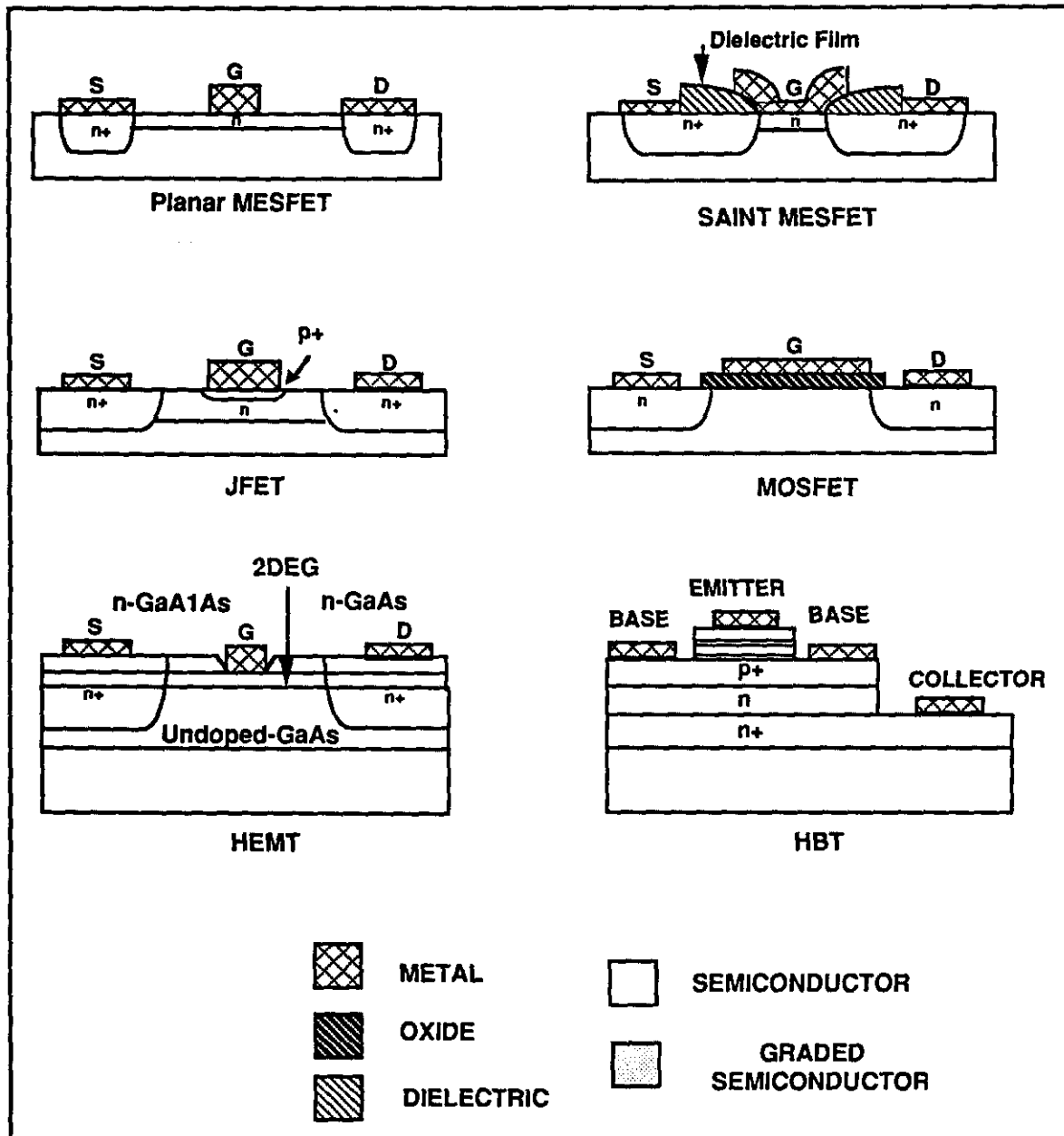
Tunnel Diodes	
Gunn Devices	
APD	Avalanche Photodiodes
CMOS	Complementary MOS devices
DHL	Double Heterostructure Lasers
HEMT	High Electron Mobility Transistor
HIGFET	(also SISFET) Hetero-Insulating Gate FET
HJBT	(also HBT) Heterojunction Bipolar Transistor
IGFET	(same as MOSFET) Insulated Gate Field-Effect Transistor
JJ	Josephson Junction
LSSL	Lateral Surface Superlattice
MESFET	MEtal Semiconductor Field-Effect Transistor
MISFET	Metal-Insulator-Semiconductor Field-Effect Transistor
MODFET	Modulation-Doped Semiconductor Field-Effect Transistor
MOSFET	(same as IGFET) Metal Oxide Semiconductor Field-Effect Transistor
MPQW	Multiple Parallel Quantum Wires
PRESTFET	Planar-Resonant-Tunneling Field-Effect Transistor
RHET	Resonant-tunneling Hot Electron Transistor
RTFET	Resonant Tunneling Field-Effect Transistor
SAINT FET	Self-Aligned Implantation for N <sup>+</sup> -layer Technology FET
SISFET	(also HIGFET) Semiconductor-insulator-semiconductor FET
TEGFET	(same as MODFET) Two-degrees-of-freedom Electron Gas FET

Several of these devices are illustrated in the accompanying figure<sup>86</sup>.

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<sup>86</sup> See, for example, J. Mun, GaAs Integrated Circuits, MacMillan Publ. Co., NY (1988), or R. Soares, J. Graffeuil, and J. Obregon, Applications of GaAs MESFETs, Artech House, Inc., Dedham, MA (1983).

## V. COMPONENTS AND DEVICES



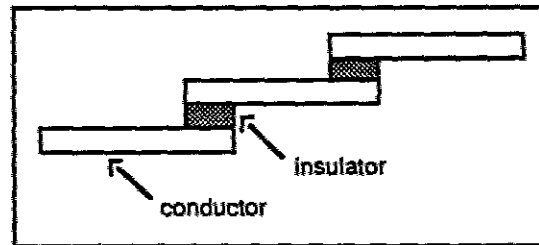
The economic and military consequences of this aspect of nanometer-dimension materials is probably greater for this application than others. Nanometer dimensional ICs will approach .25 to .1 microns by the year 2000. This is the dimension at which the standard MOS transistor will not function optimally. At this point, new design and operating principles must be introduced.

## V. COMPONENTS AND DEVICES

A massive level of activity is currently taking place at many laboratories throughout the country in examining the behavior of nanostructures having potential applicability to device fabrication. Some indication of this activity can be obtained by simply examining the wealth of information in a recent IEEE issue<sup>87</sup>. A wide variety of phenomena are being examined in these research areas. The phenomena seem to be readily predictable based on our existing knowledge of wave theory and material properties. A challenge is to demonstrate these phenomena such that the engineering of desired properties can be accomplished in a cost-effective manner. The behavior of new materials continues to represent a frontier for innovative exploration.

A significant aspect of semiconductor research is to improve the radiation resistance of semiconductor devices through structural improvements. One of the major failure mechanisms in MOS is charge migration after upset. An emerging MOS device technology is to go to CMOS on insulator. These devices are envisioned to be much more resistant to radiation damage because the insulator base does not allow collection of photocurrent transients due to radiation. Nanometer devices may respond quite differently to this mechanism, and this needs to be investigated.

Single-electron tunneling (SET) devices have become quite popular for study recently. It has been shown that tunnel junctions can be made in which the charging energy,  $e^2/2C$ , ( $C$  is capacitance) is much greater than  $kT$ . Then logic circuits can be built based on the passage of a single electron from one conductor to the next. It is equivalent to show that the voltage across a very small capacitor ( $C =$



$= \epsilon A/l$ ,  $A$  is area,  $l$  is length between plates) changes in finite increments with the passage of a single electron if the capacitance is sufficiently small. Such a device has been studied at low temperatures (e.g., 1 K), but if device dimensions can be made small enough (say, 100Å) it is thought that this phenomenon could be made to work at room temperature. Another phenomenon, quantized current, is reminiscent of the behavior of Josephson Junctions, except that the effect is due to one-electron transitions instead of two-electron transitions. The possibility of constructing logical devices is under intensive scrutiny. This device may also be a useful radiation detector. NRL has not been involved in studying the fundamental phenomenon, however the opportunity to explore the utility for devices is very attractive. A number of laboratories are pursuing this potentially useful device. Prof. Likharev at SUNY Stonybrook is very interested in pursuing this potentially important device. The American Physical Society has had several sessions on this in recent meetings. NRL finds this area attractive and is looking at this field with interest.

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<sup>87</sup> Proceedings of the IEEE, 79, (8), August (1991).

## V. COMPONENTS AND DEVICES

### **a. Memory Devices**

There are a great number of devices, materials, and systems which are utilized for the storage and retrieval of information. Included among the more common of these are computer core memory and magnetic and optical memory discs and disc systems. New improvements on the ability to pack information into smaller and smaller volumes continue to appear. This field will continue to be impacted significantly as the ability to fabricate and control the behavior of the nanometer world advances.

### **b. Cathodic Emission**

The emission of electrons from a cathode in a vacuum is highly dependent on the structure of the surface. If the surface contains structure which has a very high curvature (say with a radius of curvature of 10-25 nanometers) the emission is enhanced markedly. It is possible to consider designing cold cathodes with such designs. Devices with such performance are of particular interest for generators in the microwave or mm-wave region. The capability of constructing cathodes with nanostructures has been a relatively recent development, thus this approach to improving on the design of vacuum electronics has gained attention. Materials chosen for this application must withstand high stress fields and be relatively insensitive to surface contamination as well as be fabricated with the curvature and density of "tips" appropriate. Currently a number of methods for producing conducting and semiconducting structures on a cathode for this purpose are being explored for applicability.

## B. OPTICAL APPLICATIONS (Code 6572, 6870)

The utilization of heterojunction devices as laser sources represents a significant growth area. This is one application area which has actually developed a commercial market for products involving nanometer dimensions. Laser diodes are quite efficient. It is possible to increase the area (width of junction: 500 microns) over which electrical injection takes place in these laser diodes. By injecting a single mode optical beam into a single-pass broad area amplifier in this manner, power levels as high as 10 watts from a single laser/amplifier have been achieved (peak power, with a duty cycle of .001). Wavelengths from 0.7-1.5 microns are possible from these devices. Doubling techniques allow generation of visible radiation over a wide range of wave lengths. A prime goal in this area is an efficient laser at 910 nm, which can be then doubled to the Cesium atomic resonance filter at 455 nm (blue-green for Naval applications). The efficiency of the overall process approaches 30% for the electrical efficiency of the IR laser diodes, and 40% for the doubling process. Overall, some 10% efficiency is projected in overall system efficiency. Devices hoped for in the future would be something producing 100 mw of visible radiation in a device the size of a cigar box. These devices can be tuned (by changing diode temperature) and modulated for communications purposes. Other potential applications include optical displays, data recording, and medical applications involving laser surgery.

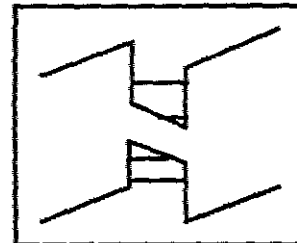


## V. COMPONENTS AND DEVICES

Beyond heterojunction lasers, the use of quantum wires and even quantum dots are being considered as active materials for future lasers. This appears attractive due to the alternate band structure in these reduced dimensional materials.

Nonlinear optical materials are being utilized for optical switching and modulation of optical signals in photonic devices. The quest for optically transparent materials having higher nonlinear optical properties has been pursued in recent years. Quantum dots seem to offer advantages for accessing the plasma resonances in both metals and semiconductors. Additional advantages of quantum dots involve the modification of the density of states due to quantum confinement effects. These modified materials should have resonances which are tunable to different energy levels by size and conductivity modifications, and offer a way to engineer optical material properties in a number of ways.

Semiconductor heterojunction materials may be fabricated with built-in strain. This strain introduces an electric field proportional to the strain (piezoelectric effect), and has been studied at NRL with GaSb/AlSb quantum well material. This can be advantageously utilized to make fast optically-induced modulators.



Nonlinear optical devices have been pursued for several years with the hope of finding materials which have low thresholds for switching when exposed to relatively moderate levels of light. Applications of materials which have high nonlinear coefficients would be in the area of integrated optics (photonics) for switching. The hope of obtaining materials which would switch quickly when exposed to damaging levels of radiation is also envisioned, although such materials need greater nonlinearity than have been observed thus far.

The utility of nanometer structures to modify the optical properties of a material leads to the concept of displays. Although liquid crystals are utilized for this purpose today, variations of this concept through special design of ferroelectric domains having nanometer dimensions is a concept being pursued.

## C. FUNCTIONAL MATERIALS

A great variety of materials appropriate for utilization due to their electronic, optical, magnetic, dielectric, and chemical properties. Many of these are discussed under the headings elsewhere in this section.

The electromagnetic properties of composites are of interest due to the modification of electromagnetic radiation reflection and absorption behavior possible. Bulk dielectric and magnetic properties not obtainable by alternative approaches are achievable through innovative design of materials having appropriate nanostructures. This includes ceramics, polymers, metal alloys, etc.

The reflection of X-Rays from a material is enhanced by utilizing materials having a variation in density which matches the wavelength of the X-Ray radiation. X-

## **V. COMPONENTS AND DEVICES**

Rays are typically less than 10 nm in dimensions. Materials can be prepared and utilized appropriate for this application.

Another functional property sought after by the Navy is one which will prevent fouling on the hulls of ships. Innovative approaches to new materials having controlled release characteristics can be introduced with nanostructures in composites.

### **D. SENSORS**

#### **1. UTILIZING PROXIMAL PROBES** (Code 6170)

Accelerometers have been made using several basic concepts and proximal probes. IR sensors have been made using the "expanding drum" concept, in which the thermal expansion of a material heated upon exposure to electromagnetic radiation changes the dimensions of a material probe. This dimensional change is sensed by a proximal probe, resulting in detection of a signal.

The identification of single molecular species is envisioned by placing probes such as monoclonal antibodies attached to proximal probe tips. Such devices may ultimately be able to probe the presence of a few chemical reactions and give rise to sensitivities and selectivities heretofore unknown.

#### **2. MAGNETIC SENSORS** (Code 6345, 6800)

The magnetic properties of materials made with nanodimensions are attracting a great deal of attention due to the much greater effects observed than for conventional magnetic materials. The spin polarizations are much greater, for example. Coupled with piezoelectric materials, devices can be made which are much more sensitive for sensing minuscule bits of information from magnetic storage devices.

The utility of Superconducting Quantum Interference Devices (SQUIDS) have been pursued for some time. The heart of this device is a Josephson Junction which has nanometer dimensions.

#### **3. ELECTROMAGNETIC SENSORS**

The use of ferroelectric films operating near the ferroelectric transition temperature could lead to sensitive detectors of electromagnetic radiation which is absorbed by the film. In particular, pyroelectric detectors of IR radiation are anticipated with the suitable fabrication of such films.

## V. COMPONENTS AND DEVICES

### 4. SUPERCONDUCTING SENSORS

The field of superconducting sensors has been reviewed by NRL researchers<sup>88</sup>. The bolometric response of changing resistance due to small temperature changes at the edge of the transition temperature appeared to offer sensitivity advantages over other detectors. This appears to be true at long IR wavelengths, and such a detector may offer additional advantages due to the response at a wide range of wavelengths. Josephson junction detectors show advantageous sensitivities at microwave frequencies. Various flux motions can be observed by optical observations near the transition temperature.

### 5. BIOCHEMICAL SENSORS (Code 6090)

One of the more imaginative and demanding programs which has attracted a good deal of attention is that of a receptor-based biosensor which will be sensitive to molecular species which would interfere with normal living functions. Such a device would be sensitive, for example, to any nerve agent which interfered with neuron transmission (rather than to a specific agent, whose detection could be circumvented by switching to another agent). Progress is being made at NRL in assembling arrays of cells (say, for example, muscle cells) which can then be queried by sensing an electrochemical potential associated with each cell. Such a device could be a neurotoxin detector. By combining such devices with neural patterning, synthetic biological components could be made which simulated the nervous structure in a living species. Neuron dendrites could be used to probe the synapse region, critical to the propagation of nerve impulses. Probes as small as 1-10 nm are needed to develop these techniques.

Antibody-antigen interactions between biological molecules are sufficiently strong and specific that this type of chemical reaction is likely to be observed with single-molecule sensitivity (see the section on Proximal Probes, above).

### 6. ELECTROCHEMICAL PROBES

"One of the most exciting potential applications of ultramicroelectrode ensembles is in the area of chemical sensors. ... ensembles can electrochemically sense significantly lower concentrations of electroactive analyte molecules than can electrodes of macroscopic dimensions. ... ultramicroelectrode ensemble-based sensors show lower

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<sup>88</sup> S. A., Wolf, U. Strom, and J. C. Culbertson, Visible and Infrared Detection Using Superconductors, Solid State Technology, pp 187-191 (1990).

## V. COMPONENTS AND DEVICES

detection limits than analogous sensors based on conventional electrodes."<sup>89</sup>

Ion-sensitive field-effect transistor (ISFET) to monitor pH values mentioned; Schottky barriers are very sensitive to diffusion of species in (or by) the layers.

### 7. FIELD EMITTER ARRAYS

Small conducting whiskers from a metallic surface can emit electrons for applications ranging from flat panel displays, high definition - high brightness TV, and vacuum microelectronics in general. An application which is pursued by several programs at NRL relates to constructing an efficient cold cathode for vacuum electron devices. This is important for microwave oscillators. Lithographic techniques utilized in support of micro/nano electronics can also be utilized in support of alternative objectives such as those of field emitter arrays.

### E. MICROMACHINES

Now that the processes are available for making a large number of 1) sensors, 2) actuators, and 3) computer-controlled closed loop devices, a new world of self-controlled "smart systems" is becoming available. Applications of micromachines appear to be unfolding as the capability for fabricating these devices and systems develops. Accelerometers are being introduced into the automobile industry for air bag deployment. Micromanipulators, piezoelectric-impact drive systems are envisioned. Microactive catheters using shape memory alloys are possible. A prototype 500x500 micron<sup>2</sup> integrated optical micro-encoder has been made at NTT Applied Electronics Laboratories.

Microlithographic techniques have been utilized to fabricate "velcro" in micron-sized binders, suitable for joining tissue associated with medical operations on patients.

An imaginative concept is one which would utilize micromachines to make chemical reactors on a chip. With such "laboratories," very small amounts of drugs might be synthesized, or a large number of parameter variations could be explored with a relatively minimal investment in materials or time to carry out the reactions (accomplished through computer control of the micromachines).

One mode of production for micromachining is the utilization of thick layers of PMMA resist, patterning the PMMA, with subsequent galvanic deposition of nickel in

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<sup>89</sup> Nano- and Micro-Structures in Chemistry, Electrochemistry, and Materials Science, ... C. R. Martin, M. J. Tierney, I. F. Cheng, L. S. Van Dyke, Z. Cai, J. R. McBride, and C. J. Brumlik (Texas A&M); in M. A. Reed, and W. P. Kirk, Nanostructure Physics and Fabrication, Proceedings of the International Symposium, College Station, Texas, March 13-15, 1989, Academic Press, N.Y., (1989). NRL Library QC 176.8 .E4 N32 (1989).

## V. COMPONENTS AND DEVICES

the etch pits. This technique has been utilized to make supersonic nozzles with a curvature of 3 microns, useful for the isotope separation of uranium.

Biological systems are replete with examples of what can be done with sensors, actuators, and logic (the behavior of organisms). Active suspensions for automobiles can be conceived. Active boundary layer control becomes a possibility. With these miniature devices, shaping can take place to accommodate nerve growth to electronic stimuli, introducing concepts associated with prosthesis, or the "bionic man," popular as a children's show two decades ago.

The micromachining techniques have recently fabricated a tunneling tip (for STM) of silicon, making use of the crystallographic planes of the silicon, to ostensibly make a "perfect" one-atom tip (some observers question this) with a high degree of reproducibility. It is possible to design hundreds (or thousands, perhaps) of tunneling tips for the purpose of writing raster information on a chip. This is conceived of as a method of achieving resolution below 0.1 micron with sufficient processing speed to reduce costs of nanoelectronic devices through parallel processing of the products.

An idea to be pursued involves making a metering valve with some 10,000 miniature valves in parallel. Each of the valves would be able to open or close individually. Such a device would be able to adjust the flow rate digitally, and would compensate for the loss of individual valves through self-sensing and actuation. This would result in a metering valve having the useful property of "graceful degradation." It should be recognized that the flow of fluids through such small diameters does not follow normal models such as the Navier-Stokes equation due to the fact that mean free paths are comparable to the dimensions of these miniature channels.

Inspection and repair in extremely tight places might be possible with components made from micromachines.

Applications for optical "circuits" are envisioned for several purposes. Variable directional coupling for optical waveguides are conceivable with these micromachined devices. Making an optical crossbar switch to provide communication between two operating microelectronic devices appears feasible, and could compete with those utilizing nonlinear methods of switching the position of optical beams.

The use of micromachines in medical technology is anticipated for a variety of purposes. Cellular manipulation, separation, and injection of cells are proposed. Microsurgery is envisioned. Artificial organs in the body may be possible. One ultimate concept, highly speculative, is that of a "robot in the bloodstream," scouring excess plaque from artery walls.

## VI. ULTIMATE UTILITY

A variety of applications involving nano-materials has been suggested in a number of sources, some of which have been mentioned in the above text. It is most appropriate to examine the current thrusts as they are espoused by the Office of the Secretary of Defense. Current focus by this office appears to be on seven S&T thrust areas:

1. Global surveillance and communications, focused on a theater of operations with sufficient fusion and planning assets.
2. All-weather, day/night precision strike against 21st century critical mobile and fixed targets.
3. All-weather defense against very low observable cruise missiles, ballistic missiles and aircraft.
4. Undersea superiority against open ocean, coastal and regional threats posed by advanced, stealthy nuclear and non-nuclear submarines and by undersea mine warfare.
5. All-weather, day/night, survivable, mobile, and lethal ground combat vehicles.
6. Technology for Training and Readiness, including embedded training, distributed simulation, and virtual environment depiction.
7. Reduction of DoD acquisition time and cost while improving performance.

This list will be interpreted by numerous planning teams, all pursuing the most important mechanisms to realize the ultimate goals implied in this list of seven thrusts. Upon reflecting on this list, it is clear that there is a major emphasis on sensing and information processing. The emphasis on "all-weather" is clearly recognition that sensors must operate under night-time or inclement weather conditions. This requires the utilization of improved sensors and/or alternate electromagnetic and acoustic wavelengths. The emphasis on stealth and counter-stealth again will be met with specialized materials, improved sensors, and with enhanced information processing, data fusion, etc. Technology for training and readiness will rely heavily on improved computational and modeling techniques in order to simulate the environment without expensive training in the actual environment for all cases. Improved transmission of information, highly dependent on computers, is a likely solution to the reduction of acquisition time. The list is clearly pointing to many of the elements expected to improve as a result of enhanced performance expected from nanostructures.

## **VI. ULTIMATE UTILITY**

### **A. INFORMATION RETRIEVAL AND PROCESSING**

#### **1. ELECTRONICS**

The applications of electronic devices are too numerous to outline here with any degree of completeness. NRL emphasis involves many aspects of electronic devices having ultimate utility in rf, microwave, and high frequency systems. This is perhaps the highest priority product desired from DoD from nanofabricated devices.

Signal processing will improve significantly by the trend to nanoelectronic devices. Functions involving adaptive filters, analog neural networks, EW signal processors for detector arrays, etc. will benefit considerably. Concepts involving distributed memory may develop with neural network approaches. Quantum interference devices, etc. are yet to be developed and offer considerable opportunity for exploitation.

As the size of the devices fabricated for nanoelectronics become smaller and smaller, the "wiring crisis" becomes a major limitation to the functioning chip. The greater density of leads having higher resistance due to smaller dimensions eventually leads to a prohibitive arrangement of connections to each function component on a chip. A proposed architecture which will possible operate to circumvent this limitation is that of cellular automata. By arranging computational modules adjacent to one another, with the ability to pass information among themselves, many computational problems will be solved with such an architecture.

#### **2. SENSORS AND SYSTEMS**

The integration of the many materials, sensors, and devices possible with nanostructures can lead to enhanced performance of a wide variety of sensors and systems, operating in a "smart" mode with logic adjacent to the sensors of the system, leading to the gathering and reduction of massive amounts of data, with the essence of the important information transmitted to a decision maker. This includes the wide variety of sensors discussed above, from field and motion sensors, chemical/biological sensors, light/electromagnetic radiation sensors, etc. and the wide variety of information processors which will be attached to the resulting signals.

### **B. PLATFORM AND WEAPONS CONSTRUCTION (Code 6300)**

#### **1. STRUCTURAL MATERIALS**

It seems clear that smaller grain sizes in metals, alloys, and ceramics should lead to stronger materials. This general statement, however, may be tempered with the observation that many such materials will undergo grain ripening at higher temperatures, with a consequent change in the desired properties. The exact nature of this process is not fully understood, which makes this an area for further investigation. Further, simply making the desired materials is a major accomplishment in many cases.

## **VI. ULTIMATE UTILITY**

The applications which can evolve with structural materials which demonstrate higher performance are too numerous to list. The observation remains that if the higher performance can be achieved on a cost-effective basis, there will be many applications for these materials. These applications will take on the form of thin films and coatings, strength-bearing ceramics, cutting tools, impact resistant structures, cements, adhesives, composites, ceramics (e.g. new generation of internal combustion engines), engineering ceramics for turbine blades, and many others.

### **2. PRECISION MACHINING**

Abrasives are characteristically made by forming composites with hard particles imbedded in a matrix. The smaller the particles, the smoother the site resulting from abrasive action. Thus the opportunity for improved abrasives for polishing is enhanced by appropriately preparing nanometer-sized materials for this purpose.

Surface roughness of a machined surface can be measured typically to less than 0.3 nm (or even factor of 10 finer!) (with light measurements, however, lateral resolution is on the order of the wavelength of light)

Precision machining of optics, particularly in the IR, was introduced in the 1970s. Diamond-turned optics was introduced in about 1977. This aspect of nanometer-precision has been under way for a number of years, and, although it has had substantial impact in machining directly optical components which high precision, substantial growth of this area is not foreseen in the near future.

Ion beam machining has a resolution limit of about 0.1 micron for acceptable removal rates.

### **3. ADHESION**

The finer grain, the thinner the adhesive layer, consequently the higher the bond strength of adhesives used to bond surfaces which are closely matched in dimensions.

### **4. FRICTION AND WEAR**

Understanding how interfaces behave at close tolerance is an open field; this is where scientific questions are coming from a technology area which has been studied for decades. The tools are now available to investigate behavior on a localized basis which have not been available before.

## **C. PROCESSING TECHNOLOGY**

Smaller particles have a higher surface area per unit mass. Chromatography beds utilize dispersions of small particles for a stationary layer. Smaller particles could conceivably utilize smaller columns, or could yield higher separation efficiencies. This aspect has been pursued by those interested in this aspect of



## VI. ULTIMATE UTILITY

processing technology. Heterogeneous catalysis is generally sensitive to the surface area; many catalysts are clearly more effective in a highly dispersed state. Advances in the ability to prepare these catalysts will undoubtedly enhance the cost-effectiveness of a given catalyst, of interest to suppliers of particular chemicals and materials.

## **VII. NRL PROGRAMS INVOLVING NANOFABRICATION**

### **A. COLLABORATIVE PROGRAMS AT NRL WHICH ARE PRINCIPALLY "NANO" IN NATURE**

#### **1. 6.1 PROGRAMS**

##### **a. R013-01-43: Surface Chemistry**

Examining the chemical and physical nature of a surface naturally leads to the examination of nanostructural features. This Task Area includes nanochemistry and the utility of proximal probes (both tunneling microscopy and atomic force microscopy) among many other methods of characterizing surfaces. Phenomena examined include adhesion, contact formation, nanoindentation, separation, and fracture of proximal probes with a surface. Molecular dynamic simulations are undertaken for the behavior of proximal probes. The fabrication and characterization of monomolecular layers and thin organic films is included in this Task Area.

##### **b. R013-01-4F: Intermolecular and Surface Forces: Adhesion/Nanomechanics**

This ARI examines the molecular contributions to adhesion and interfacial mechanics. Molecular mechanisms to be examined with AFM, STM, and near-field optical microscopy to give a picture of the short-range forces operating on nanometer dimensions. This program has been initiated in October of 1992.

##### **c. R021-02-41: Semiconductor Materials**

This Task Area investigates a large number of methods for the fabrication and characterization of semiconductor materials. Included in some of these are heterojunction materials, quantum wires, and quantum dots having nanometer dimensions. Growth techniques such as OMVPE, MBE, ALE, ion implantation, etc. are used to grow materials such as GaAs, InP, InSb, AlGaAs, InGaAs, etc. Characterization of single layer growth behavior will utilize techniques such as RHEED, Raman and IR spectroscopy, EPR, photo- and electro-reflectance, ODMR, ballistic phonon transport, Hall effect, and time-resolved photoacoustic spectroscopy.

##### **d. R021-02-42: Microstructure Electronics**

A natural extension of microelectronics in the pursuit of smaller structures is the nanometer dimension. Many of the techniques which are considered standard in the microelectronics world are useful in the extension to the nanometer region. Monolayer superlattices of AlAs-GaAs are under investigation. Fabrication techniques include MBE, electron and ion beams. Properties are to be characterized by methods such as RHEED, LEED, Auger, photo- and cathodoluminescence, photoluminescence and photorefectance, and transport measurements.

## VII. NRL PROGRAMS INVOLVING NANOFABRICATION

### **e. R021-02-4C: Nanoelectronics**

The Nanoelectronics ARI starts in October, 1991, and involves Codes 6800 (primarily) as well as Codes 6100 and 6500. A principal objective is to obtain higher performance electronics by fabricating and utilizing nanometer-scale materials and structures.

Fabrication methods will utilize both electron beam lithography and tunneling techniques. A driving question involves uncovering the limits of nanofabrication techniques. Etching techniques are to be utilized in conjunction with other fabrication approaches. The behavior of resists, chemical, physical, and exposure limits are to be investigated. Techniques involving MBE and ALE will be utilized in the preparation of heterojunction and superlattice structures. Materials to be fabricated include quantum dots and wires.

Transport properties are clearly one of the most important properties to be investigated in this program. Properties giving rise to electrical noise, electron interference effects, quantum interference switching mechanisms, ballistic transport, electron correlation effects in transport, and boundary effects are part of the wide array of phenomena to be investigated. Nonlinear properties of quantum dots represents another phenomenon to be investigated.

### **f. R021-05-44: Silicon Microelectronics Research**

This Task Area is designed to pursue research associated with silicon microelectronics, involving materials, processing, and device/circuit design. Further extensions of microelectronics lead quite naturally to nanometer dimensions. Si/Ge heterojunction material is under examination in this Task Area. Quantum transport modeling is also under study here.

### **g. R022-01-4K: Computational Frontiers in Nanoscale Structures**

An NRL ARI entitled Computational Frontiers in Nanoscale Structures starts on 1 October 1992. This program, mainly in Code 4690, utilizes local density approximations (LDAs) for treating electron exchange and correlation, and more advanced computational models such as so-called gradient corrections to the LDA approximation, to study materials properties. For example, techniques to study the properties of small clusters (~100 atoms) and of complex solid-state materials (~20 atom unit cells) are becoming widely available throughout the theory community. More advanced computational capabilities available on large-scale parallel computers will usher in the ability to work with the intermediate region in which clusters containing many hundreds of atoms will be tractable. For bulk systems, an example of a problem which can be considered in the near future is that of treating an extended defect in an otherwise perfect material. Prediction of the properties, static, dynamic and thermodynamic is the goal of these calculations. The stability of alternative structures with interesting properties can also be predicted in many cases with these

## **VII. NRL PROGRAMS INVOLVING NANOFABRICATION**

calculations. Elastic and transport properties, as well as superconducting properties are predicted. Using these approaches, bond energies can now be calculated within 0.1 eV accuracy.

### **h. R041-06-4M: Biomaterials/Interfaces**

This ARI explores the fundamental issues associated with the molecular design and fabrication of films on surfaces. Understanding the fundamentals of wetting, adhesion, molecular order and energy transfer is expected to lead to advances in magnetic, optical, and electronic materials as well as biosensors and thin-film displays. Patterned films due to self-assembly and long-range molecular interactions will be examined with a variety of surface and nanometer-characterization tools.

# APPENDIX I

## PERSONNEL AT NRL INVOLVED WITH NANOFABRICATION AND CHARACTERIZATION

	<u>NAME</u>	<u>CODE</u>	<u>BLDG.</u>	<u>RM</u>	<u>NO.</u>	<u>ACTIVITY</u>
	Ancona, Mario	6813	208	119	72534	Theory: Approximate techniques for quantum device performance; cellular automata simulation, lithography process simulation; SiGe
	Ayers, Jack	6321	42	318	76231	Fabrication: Fine-grain metals/alloys, wires
	Bartoli, Filbert	6551	30	15	73276	Fabrication/Characterization; Optical properties: Quantum dots; nonlinear optics
	Borsuk, Gerry	6800	208	258	73525	Division; Electronics
	Botka, Nick	6860	208	202	73097	Branch; Electronics: Theory, Fabrication, Characterization
	Buot, Felix	6864	208	326	72535	Theory: Simulation of carrier transport; Nanoelectronics physics and quantum-based devices
	Calvert, Jeff	6090	207	322	71294	Fabrication, Characterization; Bio and self assembly: ARI: Molecular Engineering of (Bio)materials and Interfaces
70	Campbell, Paul	6863	208	151	73414	Characterization; Electronics: Individual (single) defects in nanostructures
	Campillo, Tony	6546	12	368	72057	Fabrication, Characterization; Optical properties: Quantum dots and wires; optical characterization
	Carosella, Carmine	4671	74	209	74800	Fabrication, Characterization: Ferrite films deposited by PLS; quartz beam accelerometers
	Chow, Moog	6090	T:843		47947	Fabrication: Inclusion in vesicles for fabrication of nanometer particle sizes
	Chrissey, Doug	4670	74	214	74800	Fabrication: PLD of superconductors, ferrite thin films
	Colton, Rich	6177	207	208A	70801	Characterization: STM, AFM, Nanochemistry, Nanomechanics, ARI, Blue Sky (ASW Sensors), Single molecule ID for CBWD
	Dobisz, Elizabeth	6864	208	145	75159	Fabrication, Characterization; Electronics: Lithographic techniques for electronic materials/devices; primarily optical
	D'Antonio, Peter	6030	35	205	73267	Characterization: STM, glasses, diamond, etc.
	Edelstein, Al	6371	42	102	72970	Fabrication: Small metallic clusters
	Faire, Tom	6090	207	378B	74302	Fabrication, Characterization; Bio, Self-assembly, Sensors: Sensors: receptor-based biosensors; neural patterning
	Friebele, E. J.	6505	12	206	72270	Fabrication: Glass composites containing quantum confined structures
	Gaber, Bruce	6090	207	108A	74304	Fabrication; Bio, Self-assembly, Sensors: "Nanomachining"

	<u>NAME</u>	<u>CODE</u>	<u>BLDG</u>	<u>RM</u>	<u>NO.</u>	<u>ACTIVITY</u>
	Gabriel, Ken	6804	A69	104	73150	using tunneling techniques; molecular patterning
	Gammon, Dan	6876	208	348	73261	Fabrication/Characterization: Micromachines
						Characterization, Fabrication; Electronic properties:
						Photoreflectance, luminescence, spin density waves, strain
						induced electric fields
	Giallorenzi, Tom	6500	215	201	73171	Division; Optics
	Glesener, John	6522	12	366	75370	Fabrication: Diamond tubules
	Godbey, David	6812	208	144	48542	Fabrication; Electronics: SiGe and InSb heterojunctions by
						MBE; Quantum wires
	Goldberg, Lew	6572	215	101	79380	Applications; Diode lasers from heterojunctions, quantum
						wires
	Grabowski, Ken	4670	74	157	74800	Fabrication, Characterization: PLD deposition of
						ferroelectric films, X-rays
	Gubser, Don	6300	42	228A	72926	Division: Materials
	Hoffman, Craig	6551	30	15	73276	Characterization; Optical properties: Superlattices of
						semiconductors for optimizing non-linear properties
	Horowitz, James	4670	74	214	74800	Fabrication: PLD of superconductors, ferrite thin films
	Hsu, Dave	6114	207	234	72742	Fabrication: Preparation of 35 nm linewidth metallic
						patterns on a substrate by CVD
71	Hubler, Graham	4671	74	156	74800	Fabrication: Deposit thin films by IBAD, optical films,
						contacts to GaAs, X-ray methods, lithography masks
	Idzerda, Yves	6345	60	302	73603	Characterization: Angle-resolved Auger scattering; Spin-
						resolved spectroscopy; circularly-polarized photon
						spectroscopy
	Jonker, Berry	6345	60	302	73603	Fabrication, Characterization; Magnetic films: Spin-
						polarized effects in semiconductors, metals, etc. Angle-
						resolved Auger scattering
	Justus, Brian	6546	12	374	72057	Fabrication, Characterization; Optical properties: Quantum
						dots, microcrystallites in glasses and zeolites
	Kafafi, Zakya	6551	12	113	74871	Fabrication, characterization: Metal and semiconductor
						clusters, nanocomposites, fullerenes, optical properties
	Karle, Jerry	6030	35	201	72665	Center; Characterization: Diffraction techniques
	Killiany, Joe	6810	208	143	72524	Branch; Electronics; Applications; Electronic device
						design/characterization; radiation hardening; analog
						signal processing devices
	Klein, Barry	4690	30	201A	72549	Theory: Clusters; electronic, thermodynamic, and
						mechanical properties
	Konnert, John	6030	35	207	73267	Characterization: Nanodiffraction techniques using electron
						beams
	Koon, Norm	6342	42	208	72360	Fabrication, Characterization, Applications: Magnetic thin
						films, magnetic memory devices

NAME	CODE	BLDG.	RM	NO.	ACTIVITY
Kub, Fritz	6813	208	127	73862	Device design, device physics, analog VLSI, SiGe devices
Marrian, Christie	6864	208	145	75159	Fabrication, Characterization; Electronics: Nanoelectronics ARI, topography
Meyer, Jerry	6551	30	13A	73276	Theory, Characterization; Electronics: Superlattices of semiconductors for optimizing non-linear properties
Michel, Dave	6326	71P	1410	72621	Fabrication, Characterization; Mechanical properties: Superplasticity using nanometer-sized crystalline materials
Murday, Jim	6100	207	108	73026	Division; Chemistry
Nagel, Dave	4600	75	300	72931	Division; Condensed matter, radiation sciences
Natishan, Paul	6322	42	122	71344	Characterization/Theory: Alloy effects; behavior of metal/oxide and oxide/solution interface; Localized corrosion
Osofsky, Michael	6344	60	120	72793	Characterization; Superconductivity: Flux pinning studied by tunneling techniques; superconducting proximity effects; single electron tunneling devices.
O'Grady, William	6171	207	221	72631	Fabrication/Characterization: of 15-30Å catalyst particles.
Pande, Chandra	6325	42	320	72744	Characterization, Theory; Mechanical properties: Electron microscopy, theory of superconductivity of nanometer particles
Peckerar, Marty	6804	A69	104	73150	Fabrication, characterization, devices; Electronics: Nanofabrication facility at NRL
Priest, Dick	6522	12	366	75370	Fabrication: Diamond tubules
Prinz, Gary	6345	60	300	72433	Fabrication, Characterization: Magnetic properties of thin films and superlattice materials
Prokes, Sharka	6864	208	245	72799	Fabrication: Porous silicon, lithographic techniques
Provenzano, Virgil	6372	42	312C	72565	Fabrication, Characterization; Mechanical properties: Nanoscale crystalline materials for increased mechanical strength
Reinecke, Thomas	6877	208	352	72594	Theory: Effect of phonons on transport properties; behavior of coupled quantum dots; high density/high excitation effects in solids
Rolison, Debra	6171	207	218	73617	Characterization: Chemical and electrochemical aspects of nanoscience; zeolites, catalysts
Ross, Mark	6112	207	255	73148	Fabrication: Work Unit: Clusters consolidated work unit
Schnur, Joel	6090	207	309	73344	Center; Bio: Self-assembly, magnetic and dielectric properties; sensors
Schoen, Paul	6090	207	378A	74301	Fabrication, Characterization, Application; Bio, Self-assembly: Lipids, tubules, microencapsulation, cold cathodes
Scott, Craig	6813	208	121	74693	Devices: SiGe devices, nanoelectronic device structures

	<u>NAME</u>	<u>CODE</u>	<u>BLDG.</u>	<u>RM</u>	<u>NO.</u>	<u>ACTIVITY</u>
	Shannabrook, Ben	6876	208	354	73692	Characterization, Fabrication; Electronic properties: Photoreflectance, luminescence, spin density waves, strain-induced electric fields
	Shashidhar, R.	6090	30	404	48424	Fabrication, Characterization; Magnetic properties, Dielectric properties, Sensors; Bio, Self-assembly: Metallized tubules, ferroelectric behavior of lipids
	Singer, Irwin	6176	207	271	72327	Characterization; Tribology: Nanocharacterization of friction/wear process
	Skelton, Earl	4683	60	114	73014	Fabrication, Characterization; Structure: Taylor wires of Bi, other materials; Characterization with synchrotron sources
	Smidt, Fred	4670	521T	1	74800	Branch; Beams: Fabrication, Characterization; Beams: Beam deposition; PLD
	Snow, Eric	6876	208	348	73261	Characterization; Electronics: Defect properties in semiconductors; STM, proximity effects as photovoltaic probes; near-field optical probes
	Soulen, Bob	6344	60	116	72395	Characterization; Superconductivity: Flux pinning studied by tunneling techniques; superconducting proximity effects; single electron tunneling devices.
73	Sprague, Jim	4672	74	212	74800	Fabrication, Characterization; Beams: Beam deposition; PLD; Nanotechniques in general; Microscope techniques
	Tang, Chamei	4791	A50	118A	74148	Characterization: Fluid flow dynamics through micropores, tubes, valves, etc.
	Thompson, Phil	6812	208	142	48541	Fabrication; Electronics: SiGe and InSb heterojunctions by MBE; Quantum wires
	Tonucci, Ron	6546	12			Fabrication, Characterization; Optical properties: Quantum dots and wires; optical characterization
	Wagner, Bob	6874	208	344	73665	Fabrication, Characterization; Electronics: The Epi-Center; GaAs; GaInSb/InAs; surface roughness
	Webb, Denis	6850	208	304	73312	Branch; Electronics: Fabrication, Characterization, Devices; Electronics: Microwave devices; heterojunction bipolar transistors
	White, Carter	6119	207	215	73270	Theory: Clusters, fullerenes; electronic and structural properties
	Whitman, Lloyd	6177	207	149	48845	Characterization, Fabrication: STM, nanolithography, atomic-scale studies of kinetics and mechanisms of surface reactions
	Wilsey, Neal	6870	208	358	73693	Branch; Electronics: Heterojunction materials, photonics, processes; defect properties
	Wolf, Stu	6340	60	315	72600	Branch; Superconductivity, Magnetism: Fabrication, Characterization; Superconductivity, magnetism, etc.



## APPENDIX II: FACILITIES

The following describes briefly the larger facilities at NRL which are utilized for fabricating and characterizing nanostructures or composites involving nanostructures.

### FABRICATION

Many of the processing techniques associated with nanoelectronics such as lithography, CVD and RIE are located in Code 6804 (See subsequent section in this Appendix regarding NRL Nanofabrication Facility).

Particle beam deposition, Ion Beam Assisted Deposition (IBAD), van der Graaf generators, etc.: Code 4670

Pulsed Laser Deposition (PLD): Code 4670

Electron lithography at NRL: JEOL nanowriter: Code 6804; (See subsequent section in this Appendix regarding NRL Nanofabrication Facility)

ECR Deposition for HgCdTe materials. (Code 4670).

Focussed Ion Beam Milling (a field emission tip with Gadolinium ions): Code 6345

Molecular Beam Epitaxy (MBE): Code 6800

A Ribar #32P MBE ("the Epi-Center"). It has two chambers, one for II-VI and one for III-V materials (connected by vacuum for transfer between chambers). This device has an Auger spectrometer (single pass, 3 Kv) and RHEED (10Kv in each chamber). It is designed to achieve uniformity over a large area, and to maintain careful thermal control. Location: 207/Room 105A, Code 6874.

VG80 ("Vacuum Generators" MBE) growth system is directly connected to the surface analysis chamber, allowing surface chemistry and physics studies using x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) on samples which have not been exposed to air. This instrument is dedicated to examining SiGe materials, with dopants of Sb, B, and Ga. It can handle 3" and 4" wafers. *Ex situ* analysis includes x-ray diffraction, photoluminescence, optically detected magnetic resonance, and electrical device performance. Code 6812

## APPENDIX II: FACILITIES

VG80 ("Vacuum Generators" MBE) growth system utilized for Ga, In, Al, As growth. This machine is utilized specifically to address questions addressing the growth of atomically abrupt (or smooth) interfaces and surfaces. It supports the Nanoelectronics ARI. Location: Adjacent to Ribar 32P; Code 6876.

Varian 360 MBE instrument, recently utilized for narrow band gap semiconductors associated with InSb and InAs. This machine is being converted to an instrument which will be used for a number of materials. Location: Bldg. 208, Rm. 207A; Code 6876

Self Assembly: Vapor condensation, encapsulation, biological recognition, Langmuir-Blodgett films, clusters, etc. replete throughout various divisions at NRL

Taylor wire fabrication. This technique is able to draw glass containing a metal core to dimensions ranging from 5 microns to several hundreds of Angstroms, depending on conditions. (Code 6320)

Ion implantation facilities. These techniques have considerable flexibility for depositing thin films (microns) of selected materials on/within surfaces. These facilities are located in Code 4670.

Rapid solidification of molten materials produces fine crystallite dimensions. (Code 6320).

Molecular beams and pulsed laser production of clusters. (Code 6110).

### CHARACTERIZATION

Microscopy at NRL: Codes 4670, 6030

TEM: Hitachi H-9000, with interpretable resolution of 1.8Å; this instrument has an acceleration voltage of 300,000 v, and is dedicated to high resolution imaging. Location: Bldg. 208, Room 154A (Code 6812)

TEM: Phillips CM-30 with 2 Å resolution "point to point" (a lattice resolution of 1.4 Å). This instrument is utilized for a number of problems. Location: Bldg. 42, Room 319 (Code 6323)

XPS: X-Ray Photoelectron Spectroscopy, Surface Science Model 100. This is a UHV instrument capable of identifying minority species at 2-5% in a depth of 3-5 atomic layers and a lateral resolution of 150 microns. Location: Bldg. 207, Rm. 362. Code 6170

Auger Spectroscopy, Perkin Elmer PHI Model 660, with a lateral resolution of 0.1 micron, depth of 2-5 atomic layers, and a sensitivity of 1-2%. This instrument also has Energy Dispersive X-Ray Analysis (EDEX) with 1 micron lateral

## APPENDIX II: FACILITIES

resolution and 1-2 micron depth resolution. It can serve as a Scanning Electron Microscopy with 200-300 Å resolution. Location: Bldg. 42, Room 128.

Nanodiffraction at NRL. The instrument utilized to examine diffraction due to an area of a few angstroms is located at Arizona State U. Code 6030

Rutherford Backscatter (RBS). This instrument is located in Code 4670.

Elastic Recoil Detection. This instrument is located in Code 4670.

Optical spectroscopy (photoluminescence, absorption/scattering, limited aperture scanning). These instruments are in Codes 6870, 6550.

Synchrotron radiation, EXAFS, etc. NRL has a beam line at the National Synchrotron Light Source (NSLS) at Brookhaven (Code 4680).

Proximal probes:

- 4672 - Sprague
- 6030 - D'Antonio
- 6090 - Gaber
- 6177 - Colton
- 6344 - Osofsky
- 6864 - Marrian

Synchrotron facility (NSLS, Brookhaven): Kabler; other ports such as Bell Labs also utilized

Optical probes for thin film characterization. A number of laser transmission, reflection, fluorescence, and luminescence phenomena are examined with instruments designed for specific experiments; Codes 6551, 6800

Angle-resolved Auger scattering: This instrument is being procured; Code 6345

Near field optical microscopy: This instrument is being procured; Code 6870

## **APPENDIX II: FACILITIES**

### **NRL NANOFABRICATION FACILITY FACT SHEET**

The Nanoelectronics Processing Facility, Code 6804, is specifically available to fabricate and examine nanoelectronic samples and devices. The following description of the facility is for the convenience of potential users.

#### **Facility Mission:**

- To provide microelectronics and nanoelectronics processing capability in support of the on-going research and development effort of the Naval Research Laboratory.
- To advance the state-of-the-art in microelectronics and nanoelectronics processing as it suits the laboratory's needs for advanced process capability.

#### **Principal Material Systems:**

Silicon, GaAs, dielectric electrooptic substrate materials.

#### **Level of Capability:**

Base processes: submicron CMOS, NMOS, CCD, GaAsFET, HEMT, silicon micromachining (tactile sensor and neural probe applications).

Minimum features sizes:

CMOS: 0.75 $\mu$ m

GaAsFET/HEMT: 0.1 $\mu$ m

Quantum effect devices 15 nm

Wafer size: 3"

Throughput: not relevant for current operation. We're not an IC fab line. We could easily accommodate 100 Si CMOS wafer-starts per week, though (if required).

Assembly: full assembly capability up to single-layer PCB application.

CAD: TEK-based 4115 operation linked to VAX 150; Sun IV running CALMA; Microvax running JEBCAD (JEOL PG language); Macintosh running DW-2000.

#### **Facility Description:**

Clean: 3000 sq. ft. @ class 1000, 1000 sq. ft. at class 100

Non-clean lab space: 1000 sq. ft.

#### **Replacement cost for facility space:**

4M\$

## **APPENDIX II: FACILITIES**

### **Key capital equipment assets (and replacement cost):**

LPCVD (4-tube stack): 1M\$  
APCVD: 0.15M\$  
RIE: 0.6M\$  
Metallization: 0.7M\$ (evaporators)  
0.5M\$ (sputtering systems)  
Optical lithography (4 headway spinners, Blue M programmed bake oven, 2  
SUSSE DUV contact printers, 4 laminar flow hoods): 0.6M\$  
Oxidation/Diffusion (4 3-tube stacks): 1M\$  
Electromask optical PG + MANN stepper: 1M\$  
Cambridge EBMF-6.5: 1.5M\$  
JEOL nanowriter: 2.3M\$  
Plate contact printer, automatic plate development and etch: 0.4 M\$  
CAD/VAX: 1M\$  
Assembly (4 wirebonders, 1 wafer saw, wafer scribe): 0.6M\$  
Testing (electrical/optical): 0.5M\$  
Electrochemistry (platers, 2 laminar flow hoods): 0.2M\$

Total: 12.05M\$

### **Near Term Plans (0-5 years):**

#### **Capital equipment:**

6" Line furnace renovation (500K\$); cyclotron RIE metal etcher  
(250K\$; resist imaging SEM (250K\$); dedicated evaporators for lift-  
off (150K\$)

Facilities: Modular cleanroom addition to photo area, 200 sq. ft. (500K\$)

Photovoltaic probe .....	32	Sensitivity .....	12-13, 32, 51, 60, 75
PL .....	5	Sensors .....	3, 12, 14, 22-23, 48, 59-64
Planar-resonant tunneling field-effect transistors .....	43	Serial production .....	10
Plasma excitation .....	36	SET .....	16, 31, 56
Plasmas and beams .....	2, 16	Sherby, O. ....	53
Platinum .....	8, 37	Si/Ge .....	6-7, 68
PLD .....	2, 8, 74	Si/Si <sub>3</sub> N <sub>4</sub> .....	16
PMMA .....	10-11, 13-14, 17, 61	SiGe .....	6-7, 74
Polymethyl Methacrylate .....	10	Silicon carbide .....	13, 24
Polysilicon .....	14	SIMS .....	34, 37, 74
Porous silicon .....	36	SiN .....	16
Positron lifetime spectroscopy .....	2, 37	Single Electron Tunneling .....	56
Precision machining .....	3, 65	Sintered powders .....	49
PRESTFET .....	43, 54	Spin density waves .....	36
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